Steam Reforming of Biodiesel By-Product Glycerol

John E. Kent
Worcester Polytechnic Institute

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Steam Reforming of Biodiesel By-Product Glycerol

A Major Qualifying Project Report

Submitted to the Faculty of the
WORCESTER POLYTECHNIC INSTITUTE

in partial fulfillment of the requirements for the
Degree of Bachelor of Science
in Chemical Engineering

Submitted by:

______________________________
John Eamon Kent
April 25, 2013

Approved by:

________________________________________
Prof. Dr. Anthony G. Dixon, Advisor
Abstract

Glycerol is a by-product of the transesterification reaction used to produce biodiesel. Over the past decade, the production of biodiesel has greatly increased resulting in an oversupplied glycerol market and a reduction of its value. The biodiesel industry can add value to their glycerol by-product by steam reforming it to produce hydrogen. This project simulates glycerol steam reforming in an industrial size fixed bed reactor using computational fluid dynamics to understand its transport limitations and commercial feasibility.
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Nomenclature

\( A_c \)  cross-sectional area of tube
\( C_{ib} \)  bulk fluid concentration of species i
\( C_{is} \)  catalyst surface concentration of species i
\( C_p \)  heat capacity at constant pressure
\( D \)  tube diameter
\( D_{eff} \)  overall effective diffusivity
\( D_{ij} \)  binary diffusivity of species i and j
\( D_{sm} \)  multicomponent diffusivity
\( D_{sm,e} \)  multicomponent effective diffusivity
\( D_{K,e} \)  effective Knudsen diffusivity
\( d_p \)  catalyst particle diameter
\( G \)  superficial mass velocity
\( k_c \)  mass transfer coefficient
\( K_i \)  adsorption constant of species i
\( k_{ran} \)  reaction rate constant
\( P_c \)  critical pressure
\( P_i \)  partial pressure of species i
\( T_c \)  critical temperature
\( T_r \)  reduced temperature
\( v \)  volumetric flow rate
\( W \)  catalyst weight
\( X \)  conversion
\( x_i \)  mass fraction of species i
\( y_i \)  mole fraction of species i
\( z \)  reactor length

Greek Letters
\( \varepsilon \)  change in total number of moles for complete conversion/total number of moles fed to the reactor
\( \eta \)  effectiveness factor
\( \phi \)  porosity
\( \tau \)  tortuosity factor
\( \lambda_m \)  multicomponent thermal conductivity
\( \eta_m \)  multicomponent viscosity
\( \mu_r \)  reduced viscosity
\( \nu_i \)  diffusion volume of species i
\( \mu \)  Absolute viscosity
\( \rho \)  fluid density
\( \rho_c \)  catalyst density
Executive Summary
For the past decade, the production of biodiesel has significantly increased along with its by-product, glycerol. Biodiesel-derived glycerol massive entry into the glycerol market has caused its value to plummet. Newer ways to utilize the glycerol by-product must be implemented or the biodiesel industry will face serious economic problems. The biodiesel industry should consider steam reforming glycerol to produce hydrogen gas. Steam reforming is the most efficient way of producing hydrogen and there is a lot of demand for it in the petroleum and chemical industries.

This study investigates the feasibility of glycerol steam reforming in an industrial sized fixed bed reactor. Previous studies about glycerol steam reforming conducted experiments in micro-reactors where the transport limitations are negligible. In this report, using computational fluid dynamic (CFD) simulations, the extent of the transport resistances that would occur in an industrial sized reactor can be visualized.

An important parameter in reactor design is the size of the catalyst particle. The size of the catalyst cannot be too large where transport resistances are too high, but also not too small where an extraordinary amount of pressure drop occurs. The goal of this project is to find the best catalyst size under various flow rates that will result in the highest conversion. Computational fluid dynamics simulated the transport resistances and a pseudo-homogenous reactor model was used to evaluate the pressure drop and conversion.

CFD simulations showed that glycerol steam reforming has strong internal diffusion resistances resulting in extremely low effectiveness factors. In the pseudo-homogenous reactor model, the highest conversion obtained with a Reynolds number of 100 ($\dot{m}=29.5$ kg/h) was 9.14% using a 1/6 inch catalyst diameter. Due to the low effectiveness factors and high carbon deposition rates, a fluidized bed is recommended as the appropriate reactor to carry out glycerol steam reforming.
Introduction
Glycerol is the 10 weight percent by-product of the transesterification reaction which produces biodiesel. Biodiesel is the renewable, sustainable, and cleaner alternative to petroleum. Non-OPEC nations have been creating mandates to promote biodiesel production so that they can rely less on foreign oil. For these reasons, biodiesel production has dramatically increased in the past decade along with the amount of by-product glycerol. Biodiesel plants are now responsible for producing the majority of glycerol. The massive contribution of biodiesel glycerol has greatly increased the supply while the demand remains same. This has caused glycerol prices to plummet. The low prices, creates an economical problem for the biodiesel industry since they are making less money off the glycerol by-product. Biodiesel plants must find newer ways to utilize the glycerol by-product to increase profits and to be more competitive with petroleum [15].

A great way of to utilize glycerol is to produce hydrogen gas by steam reforming. Unlike glycerol, there is a high demand for hydrogen since it is one of the most important compounds in the petroleum and chemical industries. Steam reforming is the most efficient and popular way of producing hydrogen gas. The reaction is very endothermic and typically occurs in a fixed bed reactor, heated by an open flame furnace with natural gas as the feedstock. Implementing glycerol steam reforming will make hydrogen production less dependent on finite fossil fuels [32].

In this project, glycerol steam reforming will be simulated with computational fluid dynamics. Computational fluid dynamics can three-dimensionally calculate the governing equations of transport phenomena and reaction inside the reactor. The information obtained from the simulations will be used to find out the feasibility of the process in an industrially sized reactor as well as possible improvements that can be implemented in future studies.
Background

Energy Situation
The modern world exists because of fossil fuels. As the modern world grows, the demands of energy have placed an ever-increasing burden upon it because of its dependency on the finite reserves of fossil fuels. Fossil fuels are an unsustainable source of energy and its continued use depends upon discovery of newer, harder to get to reserves. Coal, the most abundant fossil fuel, is expected to be exhausted in 120 years. At the current rate of production, known gas reserves will last around 59 years and known oil reserves will last around 40 years [38]. The burning of fossil fuels releases greenhouse gases which trap excess heat that would otherwise normally go back into space. This process commonly known as global warming has caused the average global temperature to rise by 1.5°F since 1880. The carbon dioxide level in the atmosphere has increased from 295 ppm in 1880 to currently 390 ppm. This past year, the United States experienced its warmest year on record [27]. The average global temperature is expected to increase by 2°F to 11.5°F by 2100. The consequences of global warming are severe. Besides increasing the earth’s average temperature, global warming will influence the patterns and amounts of precipitation, reduce ice, snow covering, and permafrost, raise the sea level, and increase the acidity of the oceans. Such changes will impact our food supply, water resources, infrastructure, ecosystems, and even our own health [17]. Consequently, there has been increased research in alternative fuels such as biodiesel.

Biodiesel: Benefits and Production
In recent years, biodiesel has received a considerable amount of attention as a promising source of alternative energy. Biodiesel is a renewable alternative fuel which has the potential to become an alternative to petroleum derived diesel. Biodiesel has a lower carbon footprint than petroleum diesel. A U.S Department of Energy study showed that the production and consumption of biodiesel reduced the amount of carbon dioxide emissions by 78.5% when compared to petroleum diesel. Biodiesel gives non-OPEC nations the opportunity to rely less on importing foreign oil to suffice their energy demands. Compression-ignition diesel engines can operate on biodiesel plus the infrastructure already exists for its distribution since a regular gas...
station can be used to dispense the biodiesel. Unfortunately, the average price of biodiesel last year was higher than diesel by $0.80 and gasoline by $0.71 [18,21].

![Figure 1: Petroleum vs. Biodiesel Prices [26]](image)

Over the years, the price of biodiesel has been consistently higher than petroleum; however, the prices of biodiesel will become more competitive as the production of petroleum decreases and with process improvements such as effectively utilizing the crude glycerol by-product. According to most sources, biodiesel provides a positive energy balance. Three times more is gained than what is needed to produce biodiesel which gives biodiesel the highest energy yield of any liquid fuel [23]. Most fossil fuels have a negative energy balance. Every unit of energy used to extract and refine crude oil into petroleum diesel only yields 0.83 units of energy [2]. Because of biodiesel’s benefits, governments around the world have been creating mandates to increase biodiesel production. In the United States, the Energy Independence and Security Act of 2007, required that 1.28 billion gallons of biodiesel be produced in 2013 [4]. Despite the higher prices, the benefits together with the push of government mandates have caused the production of biodiesel to greatly increase over the past decade. Annual biodiesel production has been projected to be more than 1.9 billion barrels by 2020 [19].
Transesterification and Separation
The most common way to produce biodiesel is by transesterification catalyzed homogeneously with usually a strong base. In this reaction, triacylglycerides which are the main components of vegetable oils or animal fats, react with typically methanol to produce fatty acid methyl esters (biodiesel) and a 10% by weight glycerol by-product. After the reaction, the mixture is allowed to settle in the reaction vessel or is pumped into a settling vessel. The glycerol phase is much denser than the biodiesel phase and settles to the bottom while the biodiesel phase rises to the top. In some cases, a centrifuge might be used to help separate the two phases. Both the biodiesel and glycerol are contaminated with left over catalyst, alcohol, and components of the feedstock whether it be vegetable oils, animal fats, or maybe even used cooking oils. Other than triacylglycerides, another component of the biomass feedstock are free fatty acids. Free fatty acids can react with the caustic catalyst to produce soap. This is an undesirable reaction because the soap inhibits the separation of the biodiesel phase from the glycerol phase. Measures are usually taken to pretreat the biomass feedstock so that the free fatty acid composition is below 2.5% of the feedstock’s weight. The glycerol phase contains a higher percentage of the contaminants. The glycerol phase is about 50% glycerol or less in composition and mainly contains water, salts, unreacted alcohol, and unused catalyst. The composition varies depending on the type of biomass feedstock and the methods used to process the

Figure 2: Global Biodiesel Daily Production [35]
biodiesel. Both the biodiesel and glycerol phases undergo further purification in order to be sold in their respective markets [20,25].

![Figure 3: Transesterification Reaction [20]](image)

The pharmaceutical, cosmetic, soap, textile, chemical, and food industries use highly purified (99.7%) glycerol as a raw material. In order to achieve this high purity product, traditionally, the crude glycerol is fractionally distilled in a vacuum. However, glycerol distillation is an expensive and energy intensive process which requires a high supply of energy for vaporization because of its high heat capacity [31]. Recently, a cheaper alternative to vacuum distillation called the Ambersep™ BD50 process was jointly developed by Rohm & Haas and Novasep. Ambersep™ BD50 uses chromatography to yield a glycerol composition of 99.5 wt %. Since the salts of the crude glycerol have been removed, ion exchange could then be used to achieve the commercial grade purity [15].

**Price of Glycerol**
The industries that consume glycerol are: pharmaceutical (18%), personal care (toothpaste and cosmetics 16%), polyether/polyols manufacture (14%), food (11%), triacetin (10%), alkyd (8%), tobacco (6%), detergents (2%), cellophane (2%), and explosives (2%). The remaining share (11%) is used in the manufacture of lacquers, varnishes, inks, adhesives, plastic synthetics, regenerated cellulose, and other industrial uses [28].
The demand for glycerol in these industries has remained relatively unchanged during the rapid growth of biodiesel production. The glycerol market has therefore become saturated resulting in a dramatic decrease in the price of glycerol. Before the expansion of biodiesel production, the price of refined glycerol cost $0.70 per pound and in 2007 went down to $0.30 per pound. While the price of crude glycerol decreased from about $0.25 per pound to $0.05 per pound. High purity commercial glycerol is becoming economically unfeasible due to the lower prices of refined and unrefined glycerol. Ways to utilize the crude glycerol must be applied to increase the market’s demand for glycerol before it becomes a disposal problem [24,40]. Profitable utilization of crude glycerol will alleviate the disposal problem and can reduce costs of the biodiesel production process by up to 6.5% [14]. Employing the glycerol by-product can reduce the net production costs of B100 type biodiesel from $0.63 to $0.35 per liter [41].

**Hydrogen**

A great way of utilizing glycerol is to produce hydrogen gas by steam reforming. Hydrogen is an important chemical in the petro and chemical industries. In the petroleum industry, hydrogen is used to remove sulfur and also to upgrade heavy crude oil. In the chemical industry, hydrogen is used to produce chemicals such as ammonia, methanol, and hydrochloric acid. Hydrogen is considered to be an important energy carrier in the future because it can be used in fuel cells. Fuel cells convert chemical energy into electrical energy by means of electrochemical reactions.
Fuel cells are more energy efficient than internal combustion engines, have no moving parts, and do not release any pollutant gases [9]. Hydrogen is currently mostly produced from fossil fuels (96%). Nearly half of hydrogen is produced by the steam reforming of natural gas [7]. Steam reforming is a highly endothermic reaction where typically a hydrocarbon or alcohol is reacted with water at very high temperatures (usually between 800 and 900 K) and low pressures. A conventional steam reformer consists of 40 to 400 tubes packed with porous solid catalysts and are heated by open flame furnaces to drive the reaction forward [32]. The tubes have an internal diameter in the range of 70 to 160 mm, tube thickness of 10 to 20 mm, and length of 6 to 12 m [22]. The catalysts generally have a diameter 3-10 times smaller than the tube [26].

Glycerol is a great candidate for steam reforming since it is a sustainable process unlike using the finite fossil fuels. Theoretically, the reforming of oxygenated hydrocarbons requires less energy than that of the hydrocarbons with a similar carbon number. For example, the steam reforming of propane (C$_3$H$_8$) has $\Delta G^{\ddagger}_{823\text{ K}} = 2.2$ kJ mol$^{-1}$ ($K_{eq} = 0.73$) while the steam reforming of glycerol (C$_3$H$_8$O$_3$) has a much lower value, $\Delta G^{\ddagger}_{823\text{ K}} = -309.3$ kJ mol$^{-1}$ ($K_{eq} = 4.2 \times 10^{19}$). For hydrocarbons, both C–O and O–H bonds have to be formed. In contrast, oxygenated hydrocarbons contain these bonds already and tend to react more easily [5].

Figure 5: Methane Steam Reformer [11]
**Steps in Heterogeneous Catalytic Reactions**
The steps involved in catalytic gas-solid reactions are the following:

1. Diffusion of reactants from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of reactants through pores of catalyst
3. Adsorption of reactants onto the catalytic surface of the pores
4. Surface reaction at the catalyst surface
5. Desorption of products from catalyst site
6. Diffusion of products through pores
7. Diffusion of products from surface to bulk

The overall rate of reaction is equal to the rate of the slowest step in the mechanism called the rate determining or limiting step [16].

**External Mass Transfer**
The first step in heterogeneous catalysis involves the mass transfer of the reactants from the bulk fluid to the surface of the catalyst pellet. In this step, the reactants must diffuse through a boundary layer which surrounds the catalyst pellet. The boundary layer is a region of laminar flow directly adjacent to the catalyst pellet whereby diffusion can only take place by molecular means. The rate of mass transfer for reactant A at a bulk concentration \( C_{Ab} \) diffusing through the boundary layer is given by

\[
Rate = k_C (C_{Ab} - C_{As})
\]

where \( k_C \) is the mass transfer coefficient which accounts for the resistance to mass transfer resulting from the boundary layer and \( C_{As} \) is the concentration of A on the external surface of the catalyst. The thickness of the boundary layer is defined as the distance from the surface of the solid to the point where the concentration of the diffusing species equals 99% of its bulk concentration. The mass transfer coefficient is inversely proportional to the boundary layer thickness (\( \delta \)) and directly proportional to the diffusion coefficient (\( D_{Am} \)).

\[
k_C = \frac{D_{Am}}{\delta}
\]

The diffusion coefficient, \( D_{Am} \), measures how well species A is diffusing through the multi-component mixture, m. The mass transfer coefficient is mainly a function of the fluid velocity...
and catalyst pellet diameter. Increasing the fluid velocity will decrease the thickness of the boundary layer and also promote turbulent conditions. If the fluid flow is laminar, all of the transport will be by molecular diffusion; but if the flow is turbulent, the mass will be transported by eddies present within the turbulent core of the stream [16,37].

**Figure 6: Effects on Boundary Layer Thickness [29]**

In this study, the mass flow rates were chosen so that the Reynolds numbers were the same for each run. The Reynolds numbers are also above the laminar region in order to prevent external mass transfer limitations. In packed beds, Reynolds numbers generally above 1,900 are considered turbulent and when they are above 200 it is deemed as an unsteady transition flow [13]. The equation used to define the Reynolds number is the following:

$$Re = \frac{d_p \dot{m}}{A_c \mu}$$

Keeping the same Reynolds numbers for each run will assure that the various catalyst sizes are undergoing similar regimes of external mass transfer. This can be observed by the Frossling correlation:

$$Sh = 2 + 0.552 Re^{1/2} Sc^{1/3}$$

where Sh and Sc are the Sherwood and Schmidt numbers.

$$Sc = \frac{\mu}{\rho D_{im}} \quad k_c = \frac{Sh D_{im}}{d_p}$$
If there is no mass transfer resistance, the concentration at the interface would be the same as that of the bulk fluid. However, if external mass transfer resistance is significant, then there is a concentration gradient outside the catalyst particle. As a result, the concentration at the pellet’s surface is lower than that in the bulk fluid. Therefore, the reaction behaves as if it is a first order reaction with the mass transfer coefficient as the rate constant [34].

**Internal Diffusion**

After the reactants cross the boundary layer, they must diffuse through the pores of the catalyst before the reaction can take place. Internal diffusion may occur by one or more of three mechanisms: bulk diffusion, Knudsen diffusion, and surface diffusion. The pores inside the catalyst are not organized, straight, and cylindrical passing right through the pellet from one end to the other. Rather, the pores are tortuous, interconnecting, have dead ends, and varying cross-sectional areas. Such properties cause the flux through the catalyst pellet to be less than if the pores were uniform and must be taken into account. The diffusion coefficients factor in the random pore paths by introducing a term called the tortuosity factor (τ) and also the porosity (ϕ) of the catalyst pellet into their equations. The tortuosity factor accounts for the varying directions of the pore paths and also the varying cross-sectional areas. Diffusivities that incorporate the tortuosity factor and porosity are called effective diffusion coefficients.

Bulk or ordinary diffusion occurs when the pores are large and the gases are relatively dense. The collisions of the molecules with the pore wall are unimportant compared to the molecular collisions in the free space of the pore. The equation for the ordinary effective diffusivity is the following:

\[ D_{im,\text{eff}} = \frac{D_{im} \cdot \phi}{\tau} \]

Knudsen diffusion occurs when the gas density is low or the when the pores are small. In Knudsen diffusion, the molecules collide with the pore walls much more frequently than with each other. The equation for the Knudsen diffusion coefficient for a porous solid is the following:
\[ D_{K,eff} = \frac{D_K \cdot \phi}{\tau} = 19,400 \cdot \frac{\phi^2}{\tau \cdot S_g \cdot \rho_p \sqrt{\frac{T}{MW}}} \]

where \( S_g \) is the total surface of the porous material, \( \rho_p \) is the pellet density, \( T \) is temperature, and \( MW \) is the molecular weight.

Surface diffusion occurs when molecules adsorbed on solid surfaces have considerable mobility and move in the direction of decreasing surface concentration. Surface diffusion cannot be significant unless appreciable adsorption occurs and the absorbed molecules are not held too strongly so that they are mobile. In this study, surface diffusion was considered to be insignificant and was not accounted for in the simulations.

The Knudsen and ordinary diffusion will be considered in the simulations and to account for both types of diffusion the following equation is used [34].

\[ \frac{1}{D_{eff}} = \frac{1}{D_{K,eff}} + \frac{1}{D_{im,eff}} \]

When the reactants enter the catalyst, they are continuously absorbing and reacting on the pore walls as they move deeper inside the pellet. A concentration gradient is therefore formed inside the catalyst pellet. Since the reaction rate is dependent on concentration, the reaction rate will be at its peak at the mouth of the pores and slow down while moving towards the center of the catalyst. To account for these intra-particle gradients, a ratio called the effectiveness factor (\( \eta \)) is commonly used which measures how far the reactants diffuse into the pellet before reacting.

\[ \eta = \frac{rate \ of \ reaction \ with \ diffusion \ resistance}{rate \ of \ reaction \ at \ surface \ conditions} \]

When a catalytic reaction has internal diffusion limitations, the reactants are only consumed on the edges of the pellet because they are moving slower through the pores than the rate of reaction. The center of the catalyst is therefore wasted since reactants can never reach it before reacting. Decreasing the pellet size will reduce the internal diffusion limitations since the
reactants will take less time diffusing into and out of the pellet interior. The net molar volume change of the reaction will also affect the internal diffusion. When there is an increase in the reaction’s molar volume there will be an increased outflow of molecules from the pores which makes it harder for the reactants to diffuse into the catalyst. On the other hand, when there is a reduction in the molar volume, internal diffusion becomes easier for the reactants. For the main glycerol steam reforming reaction,

\[ C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \]

there is a net increase of six moles for the reaction which means the internal diffusion will be negatively affected by the nature of this reaction. Increasing the temperature will also increase the internal diffusion limitations since the rate of reaction will rise. A previous MQP’s simulations showed this phenomenon [16, 33].

\[ \text{Figure 7: Effect of Temperature on Effectiveness Factor [36]} \]

**Reaction Kinetics**

The kinetic model chosen to simulate the reaction was developed by C.K. Cheng et al. The model was developed by conducting various experiments on a lab scale fixed-bed reactor containing an alumina-supported Ni catalyst. During these experiments the steam to carbon ratio was varied from 1.1 to 4 and the temperature between 723 K and 823 K. The catalyst
particles were crushed to a diameter averaging between only 90 to 140 μm to greatly limit the transport resistances in order to study the intrinsic kinetics of the reaction. Prior to the reactions, the catalysts were analyzed to determine properties such as the BET surface area and pore volume. These values were incorporated in the user defined functions for the reaction simulations. A Langmuir-Hinshelwood kinetic expression based on molecular adsorption of glycerol and dissociative adsorption of steam on two different sites (strong acid and basic sites) with surface reaction as the rate determining step was derived and assessed using the glycerol consumption rate data from the experiments.

\[
r = \frac{k_{rxn} P_G \sqrt{P_{\text{H}_2\text{O}}}}{(1 + K_G P_G)(1 + \sqrt{K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}})}
\]

The kinetic model agreed with the temperature programmed desorption analysis which indicated a strong acid site near the interface of the metal-alumina support and a basic site due to the presence of surface hydroxyl and interstitial hydroxyl species in the alumina support. Activation energies for the main components were determined since the reactions were run at various temperatures. The activation energies for the consumption of glycerol and the formation of H₂ and CO₂ were all approximately 60 kJ/mol which shows that the following reaction

\[
C_3H_8O_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2
\]

was the major source of production for H₂ and CO₂. Therefore, the kinetic model was assumed to represent this reaction. Unfortunately, the reaction rate and adsorption constants are independent of temperature. Therefore, the simulation was run isothermally at 823K since the rate data used for deriving the Langmuir-Hinshelwood rate expression was obtained at that temperature [5].

**Pressure Drop**

Industrially, the catalyst size is much larger than what C.K. Cheng et al. used in their experiments. The reason why the catalyst is larger, despite the increased mass transfer
limitations, has to do with an important parameter called the pressure drop. In gas phase reactions, the concentration of the reactants is proportional to the total pressure. When the pressure drops in a reactor, the reactant concentrations and thus the reaction rate will always be lower than in the case when there is no pressure drop. The conversion will therefore be lower because of this smaller reaction rate.

A popular equation called the Ergun equation is used to predict the pressure drop in packed beds.

\[
\frac{dP}{dz} = -\frac{G}{\rho d_p} \left(\frac{1 - \phi}{\phi^3}\right) \left[\frac{150(1 - \phi)\mu}{d_p} + 1.75G\right]
\]

The Ergun equation shows that decreasing the catalyst diameter \(d_p\) will result in a greater pressure drop. Increasing the superficial mass velocity \(G\) will also result in a higher pressure drop. Glycerol steam reforming promotes a faster volumetric flow rate and therefore a greater superficial mass velocity when compared to other reactions since there is a net increase in the total amount of moles. Not only will a faster flow rate increase the pressure drop, but it will also reduce the residence time resulting in a lower conversion.

Fluid moves in the reactor because of a pressure difference between the entrance and exit. If the pressure drops before the chemicals reach the outlet then the fluid will stop moving. Economically, there should be a minimal pressure drop since it will increase the capital and operating costs of the compressors and pumps. This can especially be a problem if there is a lot of gas recycle.

Although the pressure drop is important, mass transfer is also equally as important. When designing a reactor there must be a tradeoff between the two. For instance, the optimal catalyst size cannot be too big to have substantial internal diffusion limitations while at the same time not be too small so as to create a lot of pressure drop [16,29].
Computational Fluid Dynamics

Computational fluid dynamics (CFD) is a technology that uses numerical methods and algorithms to simulate events that involve fluid motion. CFD is used in many engineering disciplines including but not limited to aerospace, automotive, electronics, chemical, and power generation. In chemical engineering, computational fluid dynamics is a great way to understand what is occurring in unit operations such as reactors without intruding on them experimentally or perhaps the temperatures are too hot to experimentally study what is happening inside. Traditionally, fixed bed reactions are modeled with several simplified assumptions such as plug flow or treating the fluid and solid phases as a single combined pseudo homogenous phase. The problem with the classical reactor models is that they average out local phenomena which are crucial to understand when designing a reactor. CFD can be used to visualize the local phenomena three-dimensionally which provides a more fundamental understanding of transport and reaction to improve the design of reactors [12].

User Defined Functions

The CFD software, Fluent, was not specifically designed for chemical engineers and so there are difficulties simulating heterogeneous reactions. A method developed by Dixon et al called the solid particle method overcomes Fluent’s deficiencies and is used to couple the three dimensional flow around the catalyst particles to a three dimensional description of transport and chemical reaction within the catalyst particles. The solid particle method defines the
catalyst pellets in Fluent as nonporous solids so that the software maintains the correct fluid mechanics of the no slip surface flow boundary condition. Since the species cannot enter inside the catalysts, user defined scalars are employed to mimic the species’ mass fractions inside the catalyst pellets. User defined functions are then used to simulate the transport and reaction inside the catalyst particles and also to couple the external chemical species with the internal user defined scalars [12]. These user defined functions include species fluid-phase and solid-phase diffusivities, species reaction sources, a uds coupler, and a reaction heat sink. One of the species is left out for Fluent to solve for. In this study, the diffusivity user defined functions include all the equations that are used for their calculation in the subroutine. By including the equations, the diffusivity subroutines are now a function of temperature, pressure, and concentration. This is different from previous studies where the diffusivities were calculated with Mathcad® under inlet bulk conditions and left as a constant value in the subroutine.
Methodology

CFD Simulations
The commercial CFD software, Fluent 6.3, was used to three-dimensionally simulate the transport phenomena and reaction of glycerol steam reforming. Two sets of CFD simulations were conducted. The first set looks at the internal diffusion limitations and effectiveness factors. The second set simulates the extent of the external mass transfer resistances.

The internal diffusion set simulated nine different spherical catalyst diameters which were 1, 1/2, 1/4, 1/8, 1/16, 1/32, and 1/64 inches. Rather than create nine different models, the original model was scaled down in order to simulate the smaller catalyst sizes. The Reynolds number for these runs was in the unsteady transition flow region (Re=683) to limit external mass transfer resistances.

The external mass transfer set consisted of one run which was simulated under laminar flow (Re=100) with a 1 inch spherical catalyst diameter. This run examines the width of concentration boundary layer and also if the lower catalyst surface concentrations had any major effect on conversion.

Geometry
A 120° wall segment (WS) model developed by Dixon et al was used for the glycerol steam reforming simulations. Running simulations through the WS rather than the whole tube will reduce the computational time while still bringing about accurate results. The wall segment is packed with spherical catalyst pellets that are one inch in diameter. The model has a porosity of 0.415 and a tube to catalyst diameter ratio of four. The geometry contains approximately 1.8 million control volumes. Smaller control volumes are located near the sensitive region where the particle-particle and particle-wall almost contact each other [12].

In order to account for the full cross-sectional area of the fixed bed, the inner side walls of the wall segment model have symmetry boundary layers. The top and bottom surfaces are identical, so that the geometry varies in a repeating manner in the axial direction. Designing the geometry in this way will result in nonreacting periodic flow conditions where the flow patterns repeat and the pressure drop would be constant if numerous wall segment models were lined
up against each other. The nonreacting periodic flow conditions can be used to create a velocity profile. This profile can then be used as a realistic inlet velocity rather than an unrealistic uniform inlet velocity when reacting nonperiodic flow is occurring [10].

Figure 9: Wall Segment Geometry [10]

Operating Conditions and Settings
All the simulations modeled the conditions at the entrance of a glycerol steam reformer. The conditions shared by all the simulations are given in Table 1.

Table 1: CFD Reactor Conditions and Properties

<table>
<thead>
<tr>
<th>Phase</th>
<th>T [K]</th>
<th>P [kPa]</th>
<th>ρ [kg/m³]</th>
<th>c_p [J/kg·K]</th>
<th>λ [W/m·K]</th>
<th>μ [Pa·s]</th>
<th>x_{G,0}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid</td>
<td>823</td>
<td>101.325</td>
<td>0.3703</td>
<td>2211</td>
<td>0.0716</td>
<td>2.74 × 10^{-5}</td>
<td>0.362</td>
</tr>
<tr>
<td>Solid</td>
<td>823</td>
<td>1947</td>
<td>1000</td>
<td>1.0000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The inlet glycerol mass fraction (x_{G,0}) corresponds to a steam to glycerol molar ratio of 9:1. This ratio was suggested by Adhikari et al since it will improve hydrogen yield and also minimize carbon formation. Water and glycerol were the only compounds entering the reactor. Adhikari et al also suggested that the operating pressure be atmospheric since increasing pressure will reduce hydrogen yield by promoting methane production [1]. Industrially, the inlet pressure
will probably be slightly higher than atmospheric pressure to account for pressure drop unless there is a vacuum at the outlet of the reactor. The inlet operating temperature is 823 K considering that is the temperature the isothermal rate law corresponds to. This is also a reasonable temperature since a study by Chiodo et al showed that hydrogen yield reaches its maximum at 923 K, and at even higher temperatures encapsulated carbon is formed which immediately deactivates the catalyst [8]. Correlations were used to determine the heat capacity (cp), thermal conductivity (k), and viscosity (μ) of the fluid. The solid phase in the model represents the catalyst pellets which are made of alumina (Al₂O₃).

The 3D pressure-based solver was used with the SIMPLE scheme for pressure-velocity coupling, absolute velocity formulation, the Green-Gauss cell based gradient option, implicit formulation, steady time, first-order discretization, and superficial velocity porous formulation. The under-relaxation factors were left at their default values unless there was instability in the iterations in which case they were reduced.

The difference between the internal diffusion runs and the laminar run pertains to the Reynolds number and also the type of viscous model used. The internal diffusion runs had a Reynolds number of 683 while the laminar run had only 100. The internal diffusion runs used the SST k-omega model while the laminar run used the laminar model.

**Computational Procedure**

For all the CFD simulations, a non-reacting periodic flow simulation was performed before the actual reaction simulation. The flow profile was saved and used as the inlet boundary condition in the reaction simulation. This was done so that the inlet flow was more realistic. The flow profile contained the x, y, and z velocities, the turbulent kinetic energy, and the specific dissipation rate. The laminar flow profile only had the x, y, and z velocities. Unlike the flow simulation, the reaction simulation did not have the periodic flow restriction. The reaction simulations were gradually started up in order to avoid runtime errors. The equations that the simulation solved for were gradually enabled. For instance, the simulation started out with the flow and turbulence equations enabled and then the user-defined scalar equations were enabled every 100 iterations. The laminar reaction simulation obviously only began with just
the flow equation enabled. A procedure known as “bootstrapping” was also employed when starting up the reaction simulations to prevent runtime errors. In the bootstrap procedure, the reaction rate is controlled by changing the density of the catalyst. Initially, the catalyst density is at 1% of its value and then is gradually increased once all the simulation’s equations are enabled.

The periodic flow simulations typically converged in 1,500 iterations while the reaction simulations took around 5,000 iterations. The flow simulations were considered converged when the residuals dropped below the required values. For the reaction simulations, instead of following Fluent’s standard for convergence, a define on demand function was used that calculated the catalyst particle’s reaction rate. Convergence was observed when the reaction rates in the catalysts no longer changed.

**Pseudo-Homogenous Model**
A pseudo-homogenous model was developed using MATLAB to give a macroscopic view of what is happening in the entire packed bed reactor rather than just a small segment which is what the CFD simulations accomplished. The CFD simulations do an excellent job showing the transport phenomena, however in such a small segment it is hard to get a good picture of what the pressure drop and conversion will be down the length of the reactor. When deciding on the best catalyst size for maximum conversion, there is a balance between pressure drop and mass transfer. The pseudo-homogenous model will show what this optimum catalyst size is and how much conversion can be achieved.

**Operating Conditions**
The operating conditions are similar to the CFD simulations except the inlet pressure was increased to 2 atm to account for the pressure drop. Three different Reynolds numbers were simulated 100, 200, and 300. The reactor dimensions are also different since the tube diameter is kept constant at 5 inches. The length of the reactor is 12 meters.
Governing Equations
A pseudo-homogenious model treats the solid catalysts and the fluid as one phase and uses correlations to describe various phenomena occurring inside the reactor. The core of this particular pseudo-homogenious model is the two differential equations that are solved simultaneously by MATLAB.

\[
\frac{dy}{dW} = -\alpha (1 + \varepsilon X) \quad \frac{dX}{dW} = -\frac{r_0' \cdot \eta}{F_{A0}}
\]

The variable \( y \) is the ratio of the instantaneous pressure over the inlet pressure (\( P/P_0 \)). This ratio is used to reduce the stiffness of the differential equation which calculates the pressure drop as a function of catalyst weight (\( W \)). The other differential equation computes the conversion of glycerol steam reforming with respect to catalyst weight. The mass transfer effects are accounted for in this equation by including the effectiveness factor (\( \eta \)) which was obtained from the CFD simulations.

\[
\alpha = \frac{2\beta_0}{A_c(1 - \phi)\rho_cP_0}
\]

\[
\beta_0 = \frac{G(1 - \phi)}{\rho_0d_p\phi^3} \left[ \frac{150(1 - \phi)\mu}{d_p} + 1.75G \right]
\]

The above equations are derived from the Ergun Equation which is the correlation used to describe the pressure drop in the packed bed reactor [16]. A void fraction correlation developed by Beavers et al for spherical catalysts in a tubular reactor since the void fraction was not constant because the catalyst diameter changed but not the tube diameter [3].
\[
\phi = 0.368 \left[ 1 + \frac{2d_p}{D} \left( \frac{0.476}{0.368} - 1 \right) \right]
\]

**Computational Procedure**

The MATLAB model is separated into two parts or m files: a function and script file. The script file contains all the constants, executes the ordinary differential equation (ode) solver, and post-processing calculations. The function file holds the equations that need to be solved which is inputted into the ode solver. MATLAB’s numerical differential solver, ode45, which uses fourth and fifth order Runge-Kutta formulas, was used to solve the differential equations. The function file contains an independent variable \(W\) (catalyst weight) and a vector \(x\) which contains \(X\) and \(y\). The script file sets initial conditions for the dependent variables \([0;1]\) and the bounds for the independent variable \([0 \text{ Wend}]\) needed for the ode solver. The upper bound for the independent variable is set as a variable which corresponds to the following equation where \(z\) is the length of the reactor which is equal to 12 meters.

\[W_{\text{end}} = z(1 - \phi)A_c\rho_c\]

The above equation is used so that the length of the packed bed reactor is always 12 meters. Originally the independent variable for the differential equation was \(z\) and therefore the upper bound was 12. However, the differential equations were too stiff with \(z\) as the independent variable and so \(W\) had to be used. When the differential equations are solved, the answers are organized with post-processing equations. MATLAB outputs the answers of the pseudo homogenous model in large arrays. These equations extracted and organized the essential results from the large arrays. The post-processing equations were very important since for loops were used. Rather than entering the different values for the catalyst diameter and Reynolds number manually, MATLAB did it automatically using two for loops which varied these two parameters. The essential information needed from each run is the exiting conversion and pressure. An array was created to record the Reynolds number, catalyst diameter, outlet conversion, and outlet pressure for each of the input conditions that the for loops went through. The array was sent to Excel were the information was sorted to find the maximum conversion whose exiting pressure did not drop below atmospheric for each Reynolds number.
Results and Discussion

Internal Mass Transfer
Numerous simulations were run to observe the transport limitations of glycerol steam reforming. The first set of simulations were conducted to find out the internal diffusion limitations of the reaction. The simulations were run at high velocities to minimize external mass transfer limitations and had varying spherical catalyst diameters. The catalyst diameters studied were 1, 1/2, 1/4, 1/8, 1/16, 1/32, and 1/64 inches.

![Image: 1 inch Diameter Catalyst Cross-Section of Glycerol Mass Fraction]

Figure 10: 1 inch Diameter Catalyst Cross-Section of Glycerol Mass Fraction

Figure 1 is a contour plot of the glycerol fraction inside a 1 inch diameter catalyst particle. The cross-section clearly shows that glycerol steam reforming has major internal diffusion limitations because the reactant glycerol is fully consumed only on the rim of the catalyst. Since the rate law is irreversible, the reactants are fully depleted in the center of the catalyst particle. Although the 1 inch diameter catalyst is diffusion limited, better results are expected from much smaller catalysts such as the 1/64 inch diameter pellet because internal diffusion improves with smaller catalyst particles.
As can be seen from Figure 2, there is no observable difference between the cross-section contours of the smaller and larger catalyst sizes. In order to obtain a more accurate understanding, a define on demand function was utilized which outputs the reaction rates occurring inside the catalyst particles. Next, surface integrals were calculated to find out the average concentrations of the reactants on the catalyst surfaces. The reactant concentrations on the surface were plugged into the rate expression to find out the ideal catalyst surface reaction for each catalyst size. The effectiveness factor was then calculated for each catalyst size by dividing the actual reaction rate over the ideal reaction rate at catalyst surface conditions.
The above effectiveness factors are extremely low. As a comparison, methane steam reforming which has high diffusion limitations has an effectiveness factor of 0.01 for a 2/3 inch diameter catalyst [39]. In previous methane steam reforming simulations by Dixon et al, the effective diffusivity of methane was $1.295 \times 10^{-6}$ m$^2$/s. While with glycerol steam reforming, glycerol had a better effective diffusivity with $1.342 \times 10^{-5}$ m$^2$/s. By looking just at the effective diffusivity values it would appear that methane steam reforming was more diffusion limited; however, the reaction stoichiometry tells a different story. The primary methane steam reforming reactions have a maximum net molar increase of two. The main glycerol steam reforming reaction has a net molar increase of six.

### Primary Methane Steam Reforming Reactions

- $CH_4 + H_2O \leftrightarrow CO + 3H_2$
- $CO + H_2O \leftrightarrow CO_2 + H_2$
- $CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$

As was previously mentioned in the background information, when there is a net molar increase in the reaction stoichiometry there will be an increased outflow of products from the pores which makes it harder for the reactants to diffuse into the catalyst.
External Mass Transfer
To observe the extent of the external mass transfer limitations, the largest catalyst size (1 inch diameter) was simulated in the laminar flow region (Re=100).

As can be seen by looking at Figure 3, the laminar flow case has an observable concentration boundary layer while for the unsteady flow case no boundary layer can be seen. To get a better understanding of the external phase transfer phenomenon, surface integrals were used to calculate the average surface fractions on all the catalyst particles. A define on demand function was also used that outputs the flux of glycerol into all the catalyst particles in order to calculate the mass transfer coefficient. According to the chart below, the glycerol catalyst surface fraction for unsteady flow is equal to 0.357 which is almost equal to bulk glycerol mass fraction of 0.362 indicating a very fine concentration boundary layer and a negligible external mass transfer resistance. For the laminar case, glycerol had a catalyst surface mass of 0.335. With a lower surface mass fraction, the laminar case’s reaction rate was slightly lower, but the conversion was higher than the unsteady flow case since it had a longer residence time.

Figure 12: Concentration Boundary Layer (A) Re=100 (B) Re=683
The external mass transfer resistance was also calculated for the various catalyst sizes in the unsteady flow regime. Interestingly, the glycerol surface mass fraction remained practically the same for the different catalyst sizes probably since the Reynolds number was the same for each run. From the chart below, it can be seen that the flux of glycerol into the catalysts increased as the catalyst size decreased. Although the glycerol surface fraction remained the same for all the catalyst sizes, the flux did not which caused external mass transfer resistance to decrease with smaller catalyst sizes. This coincides with reaction engineering theory.

### Table 5: External Mass Transfer Resistance vs. Catalyst Diameter

<table>
<thead>
<tr>
<th>Catalyst Diameter</th>
<th>Glycerol Flux (kmol/m²s)</th>
<th>Resistance, 1/kc (s/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.28×10⁻¹⁰</td>
<td>58,841</td>
</tr>
<tr>
<td>1/2</td>
<td>8.56×10⁻¹⁰</td>
<td>29,421</td>
</tr>
<tr>
<td>1/4</td>
<td>1.71×10⁻⁹</td>
<td>14,685</td>
</tr>
<tr>
<td>1/8</td>
<td>3.42×10⁻⁹</td>
<td>7,357</td>
</tr>
<tr>
<td>1/16</td>
<td>6.84×10⁻⁹</td>
<td>3,680</td>
</tr>
<tr>
<td>1/32</td>
<td>1.37×10⁻⁸</td>
<td>1,843</td>
</tr>
<tr>
<td>1/64</td>
<td>2.72×10⁻⁸</td>
<td>927</td>
</tr>
</tbody>
</table>

**Pseudo-Homogenous Model**

As was mentioned in the methodology, the pseudo-homogenous model was made to give a macroscopic view of what is happening in the reactor rather than just a small segment which is what the CFD simulations accomplished. Two important parameters that did not have significance in the CFD simulations were the pressure drop and conversion. These parameters will be modeled in the pseudo-homogenous model. The goal of the pseudo-homogenous model is to find the best catalyst size for a certain Reynolds number. Many factors such as heat
transfer, carbon deposition, selectivity, and economics are not accounted for in the model which plays a significant role in reactor design. Despite these shortcomings, the model will roughly show the performance of glycerol steam reforming occurring in a packed bed reactor. The pseudo-homogenous model includes the effectiveness factors obtained from the CFD simulations. A power trend line was used on the effectiveness factors data so that catalyst sizes which were not simulated with CFD could be included in the pseudo-homogenous model.

![Graph showing Effectiveness Factor vs. Catalyst Diameter](image)

**Figure 13: Effectiveness Factor vs. Catalyst Diameter**

Table 6 summarizes the results of the pseudo-homogenous model. The goal was to choose the best catalyst size that achieved the highest conversion without dropping below atmospheric pressure. The catalyst diameters in table 6 are not precisely the best catalyst size. The exiting pressure is not atmospheric so there is room for improvement. This is because only whole numbers where used in the fractions for the catalyst diameters and not decimals such 1/6.5 inches. Also, the reactor should not be designed to have an outlet pressure of exactly 1 atm. The outlet pressure should be slightly above atmospheric because the pressure drop might increase, for example if some catalysts particles break and clog up the reactor. For this model, increasing the operating pressure would increase reaction rate and thus conversion and also increase the amount of room available for pressure drop. However, in reality, previous studies
have shown that higher pressures reduce hydrogen yield and promote carbon deposition [1]. Therefore, the inlet pressure is only 2 atm to account for the selectivity and coking which is not included in the model.

<table>
<thead>
<tr>
<th>Re</th>
<th>Catalyst Diameter</th>
<th>Exiting Pressure</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1/6</td>
<td>1.40</td>
<td>9.14%</td>
</tr>
<tr>
<td>200</td>
<td>1/4</td>
<td>1.45</td>
<td>3.24%</td>
</tr>
<tr>
<td>300</td>
<td>1/3</td>
<td>1.55</td>
<td>1.68%</td>
</tr>
</tbody>
</table>

Having extremely low flow rates seems like the best way to optimize pressure drop and conversion, but other parameters have to be taken into account. Lower flow rates widen the boundary layer surrounding the catalyst pellet. Previous results showed that the boundary layer was not a problem for mass transfer, but it has been known to cause problems with heat transfer which was not simulated since the reaction rate had no temperature dependence. Heat transfer is the opposite of mass transfer in terms of transport difficulties into the catalyst particle since the boundary layer is the more resistant step. From an economic perspective, low flow rates will require more tubular reactors which will increase the capital cost.

Although this model has a margin of error, it does show that there will be very low conversion when glycerol steam reforming with a Ni/Al₂O₃ catalyst. The major reason why conversion is so low has to do with the strong internal diffusion resistances. Another reason why there is poor conversion pertains to the reaction stoichiometry where there is a net gain of six moles which increases the volumetric flow rate and reduces the residence time. As what can be seen from the equation below and figure 14, this is a minor effect because the volumetric has not increased too much down the reactor because it is a function of conversion.

\[ f = \frac{v}{v_0} = \frac{1 + \varepsilon X}{y} \]
There is going to be a large amount of recycle due to the low conversion which is going to increase compressor costs and also the capital cost will increase because more tubular reactors will be needed for the large recycle stream. Even though economics was not included in the model, steam reforming glycerol in a packed bed reactor with a Ni/Al$_2$O$_3$ does not seem very economical. Improvements must be made before this process is industrialized.

![Figure 14: Change in volumetric volume vs. z](image-url)
Figure 15: Pressure Drop vs. Reactor Length, Re = 100

Figure 16: Pressure Drop vs. Reactor Length, Re = 200
Figure 17: Pressure Drop vs. Reactor Length, Re = 300

Figure 18: Conversion vs. Reactor Length, Re = 100
Figure 19: Conversion vs. Reactor Length, Re = 200

Figure 20: Conversion vs. Reactor Length, Re = 300
Conclusions and Recommendations

This study has demonstrated that the steam reforming of glycerol in a packed bed reactor with a Ni/Al₂O₃ catalyst has strong internal diffusion resistances and low conversion. In order to arrive at these conclusions computational fluid dynamics and a pseudo-homogenous reaction model were used. The commercial CFD software, Fluent, was utilized to carry out the glycerol steam reforming simulations in a wall segment geometry filled with spherical catalysts. Seven different catalyst sizes were simulated under similar flow conditions. For all the catalyst sizes, the reaction only occurred on the outer rim of the catalyst particle. Define on demand functions were employed to calculate the effectiveness factor for each catalyst size. Values for the effectiveness factors were orders of magnitude lower than methane steam reforming. The 1/64 inch diameter catalyst only had an effectiveness factor of 4.411×10⁻⁴. The effectiveness factor for each catalyst size was plotted and strongly agreed with a power trend line. The equation for the trend line was used in the pseudo-homogenous model. The highest conversion obtained in the model was 9.14% with a 1/6 inch diameter catalyst and a Reynolds number of 100 (\(\dot{m}=29.5\) kg/h).

One way of improving the conversion is by changing the design of the catalyst. Since the reaction is mainly occurring near the surface of the catalyst, a better shape can be used to maximize the geometric surface area of the catalyst per reactor volume. A better shape can also help reduce the pressure drop in the reactor. Also, the expensive catalytic active metals (Nickel) should be placed only on the rim of the pellet because the poor diffusion will prevent the reactants from reaching the active metals in the center of the particle [29].

![Figure 20: Improved Catalyst Shapes](image)

A second way of improving the conversion is by using a different active metal. Ni/Al₂O₃ is the most popular catalyst used in steam reforming due to its good activity and low cost, however, work by Chiodo et al has shown that steam reforming glycerol is much different than other
compounds. The study discovered that glycerol is thermally unstable and portion of it is decomposing into mostly carbon monoxide and olefins before reaching the catalysts. Rh/Al2O3 was determined to be a better catalyst because rhodium can cleave the C=C bonds of the olefins and is more resistant to coke formation [8].

Finally, the third way of improving the conversion is by using a fluidized bed reactor. In fluidized bed reactors, the catalyst particle diameters can average less than 100 μm which will greatly improve the effectiveness factor. According to the power trend line equation, the effectiveness factor will be 0.01. Fluidized bed reactors also can continuously regenerate coked catalysts. Glycerol steam reforming catalysts will need this continuous regeneration. In a study by Chiodo et al, all the catalysts tested drastically deactivated from carbon deposition during the first 2 hours of reaction [8, 29].

Future studies in the field computational fluid dynamics for glycerol steam reforming should conduct simulations of a fluidized bed reactor. The kinetic expression developed by C. K. Chen for a Co-Ni/Al2O3 catalyst should be used in both fixed and fluidized bed reactor simulations. The rate of carbon deposition should be simulated. Finally, for packed bed reactors, simulations should be run with better catalyst shapes [6].
References


Appendix A: Property Correlations

Various property correlations had to be used to describe the diffusivities, viscosity, thermal conductivity, and heat capacities of the glycerol mixture composed glycerol, water, hydrogen, and carbon dioxide since the actual information was not available.

Diffusion Coefficients

Binary diffusivities of one component’s diffusion in another must be defined before the relationship on how a species diffuses in a mixture can be defined. The Fuller-Schettler-Giddings Correlation was used to calculate the binary diffusion coefficient. Keep in mind that $D_{AB} = D_{BA}$.

$$D_{AB} = \frac{0.001T^{1.75} \left(\frac{MW_A + MW_B}{MW_AM_{WB}}\right)^{0.5}}{P \left[\left(\sum \nu\right)^{1/3}_A + \left(\sum \nu\right)^{1/3}_B\right]^2}$$

Where $(\sum \nu)_A$ stands for the sum of the diffusion volume of component A. Once the binary diffusivities are calculated, the multicomponent diffusion coefficient can be solved. This was done by using the Stefan-Maxwell, Smith and Taylor correlation.

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

For this equation the ratio of the molar fluxes $(N_j/N_i)$ was assumed to be the same as the ratio of the stoichiometric coefficients. This is not correct unless the pellets are symmetrical with uniform surface conditions, which does not occur. The above correlations were used directly in both the uds_diff and uds_fluid define diffusivity udf subroutines [13, 30].
Viscosity
The Reichenberg method was used to correlate the viscosity of the glycerol mixture. The
Reichenberg method is the most complex correlation for low pressure gas mixtures, however it
has consistently been proven to be the most accurate. To use the Reichenberg correlation, one
needs, in addition to temperature and composition, the viscosity, critical temperature, critical
pressure, molecular weight, and dipole moment of each component in the mixture [30].

\[ \eta_m = \sum_{i=1}^{n} K_i \left( 1 + 2 \sum_{j=1}^{i-1} H_{ij} K_j + \sum_{j=1}^{n} \sum_{k=1}^{n} H_{ik} H_{jk} K_j K_k \right) \]

\[ K_i = \frac{y_i \eta_i}{y_i + \eta_i \sum_{k=1 \neq i}^{n} y_k H_{ik} [3 + (2M_k/M_i)]} \]

\[ U_i = \frac{[1 + 0.36T_{ri}(T_{ri} - 1)]^{1/6} F_{Ri}}{(T_{ri})^{1/2}} \]

\[ C_i = \frac{M_i^{1/4}}{(\eta_i U_i)^{1/2}} \]

\[ F_{Ri} = \frac{T_{ri}^{3.5} + (10 \mu_{ri})^7}{T_{ri}^{3.5}[1 + (10 \mu_{ri})^7]} \]

\[ T_{ri} = \frac{T}{T_{ci}} \]

\[ \mu_{ri} = 52.46 \frac{\mu_c^2 p_{ci}}{T_{ci}^2} \]

\[ H_{ij} = \left[ \frac{M_i M_j}{32(M_i + M_j)^3} \right]^{1/2} (C_i + C_j)^2 \times \frac{[1 + 0.36T_{rij}(T_{rij} - 1)]^{1/6} F_{Rij}}{(T_{rij})^{1/2}} \]

\[ H_{ij} = H_{ji} \]
\[ T_{rij} = \frac{T}{(T_{ci} \cdot T_{cj})^{1/2}} \]

\[ F_{Rij} = \frac{T_{rij}^{3.5} + (10 \mu_{rij})^7}{T_{rij}^{3.5} \left[ 1 + (10 \mu_{rij})^7 \right]} \]

\[ \mu_{rij} = \sqrt{\mu_{ri} \mu_{rj}} \]

**Thermal Conductivity**

Wassiljewa Equation [30]

\[ \lambda_m = \sum_{i=1}^{n} \frac{y_i \lambda_i}{\sum_{j=1}^{n} y_j A_{ij}} \]

\[ A_{ij} = \frac{\varepsilon[1 + (\lambda_{u_i} / \lambda_{v_i})^{1/2}(M_i / M_j)^{1/4}]^2}{[8(1 + M_i / M_j)]^{1/2}} \]

\[ \lambda_{ui} = \Gamma_i \left[ \exp(0.0464T_{ri}) - \exp(-0.2412T_{ri}) \right] \]

\[ \lambda_{uj} = \Gamma_i \left[ \exp(0.0464T_{ri}) - \exp(-0.2412T_{ri}) \right] \]

\[ \Gamma = 210 \left( \frac{T_c M^3}{P^4} \right)^{1/6} \]

**Heat Capacity**

\[ C_{p,m} = \sum_{i=1}^{n} x_i C_{p,i} \]
Appendix B: Property Correlation Calculations

Diffusion Coefficients

Molecular Weights [g/mol]

\begin{align*}
\text{M}_{\text{h}2} & := 1.007942 \\
\text{M}_{\text{co}2} & := 44.0 \\
\text{M}_{\text{h}2o} & := 18.015 \\
\text{M}_{\text{gsr}} & := 92.0938 \\
\end{align*}

Atomic and Structural Diffusion-Volume Increments [cm³/mol]

\begin{align*}
\text{v}_{\text{h}2} & := 7.0' \\
\text{v}_{\text{co}2} & := 26.5 \\
\text{v}_{\text{h}2o} & := 12.5 \\
\text{v}_{\text{gsr}} & := 3 \cdot \text{v}_{\text{h}2} + 8 \cdot \text{v}_{\text{co}2} + 3 \cdot \text{v}_{\text{h}2o} = 81.78 \\
\end{align*}

BET surface area

\begin{align*}
\text{S}_g & := 175100 \quad \text{cm}^2 / \text{g} \\
\end{align*}

Equivalent Pore Radius

\begin{align*}
\text{r}_p & := \frac{2 \cdot \text{e}}{\text{S}_g \cdot \rho} = 2.581 \times 10^{-7} \quad \text{cm} \\
\end{align*}

Fuller-Schettler-Giddings Correlation

\begin{align*}
\text{D}_{\text{gsr}_{\text{h}2o}} & := \frac{10^{-3} \cdot \text{T}_1^{1.75} \left( \frac{\text{M}_{\text{gsr}} + \text{M}_{\text{h}2o}}{\text{M}_{\text{gsr}} \cdot \text{M}_{\text{h}2o}} \right)^0.5}{\text{P}_1 \left( \frac{1}{\text{v}_{\text{gsr}}} + \frac{1}{\text{v}_{\text{h}2o}} \right)^2} \\
\text{D}_{\text{gsr}_{\text{co}2}} & := \frac{10^{-3} \cdot \text{T}_1^{1.75} \left( \frac{\text{M}_{\text{gsr}} + \text{M}_{\text{co}2}}{\text{M}_{\text{gsr}} \cdot \text{M}_{\text{co}2}} \right)^0.5}{\text{P}_1 \left( \frac{1}{\text{v}_{\text{gsr}}} + \frac{1}{\text{v}_{\text{co}2}} \right)^2} \\
\text{D}_{\text{h}2o_{\text{co}2}} & := \frac{10^{-3} \cdot \text{T}_1^{1.75} \left( \frac{\text{M}_{\text{h}2o} + \text{M}_{\text{co}2}}{\text{M}_{\text{h}2o} \cdot \text{M}_{\text{co}2}} \right)^0.5}{\text{P}_1 \left( \frac{1}{\text{v}_{\text{h}2o}} + \frac{1}{\text{v}_{\text{co}2}} \right)^2} \\
\text{D}_{\text{co}2_{\text{h}2o}} & := \frac{10^{-3} \cdot \text{T}_1^{1.75} \left( \frac{\text{M}_{\text{co}2} + \text{M}_{\text{h}2}}{\text{M}_{\text{co}2} \cdot \text{M}_{\text{h}2}} \right)^0.5}{\text{P}_1 \left( \frac{1}{\text{v}_{\text{co}2}} + \frac{1}{\text{v}_{\text{h}2}} \right)^2} \\
\end{align*}
Knudsen Diffusion Coefficients

\[
\text{DK}_{\text{gsr}} := 9700 \rho \left( \frac{T_1}{M_{\text{gsr}}} \right)^{0.5} \quad \text{DK}_{\text{h}2\text{o}} := 9700 \rho \left( \frac{T_1}{M_{\text{h}2\text{o}}} \right)^{0.5}
\]

\[
\text{DK}_{\text{co}2} := 9700 \rho \left( \frac{T_1}{M_{\text{co}2}} \right)^{0.5} \quad \text{DK}_{\text{h}2} := 9700 \rho \left( \frac{T_1}{M_{\text{h}2}} \right)^{0.5}
\]

Stoichiometric Ratios

\[
\begin{align*}
\text{Nh}_2\text{Ngsr} & := -7 \\
\text{Nh}_2\text{O}_\text{Ngsr} & := 3 \\
\text{Nco}_2\text{Ngsr} & := -3
\end{align*}
\]

\[
\begin{align*}
\text{Ngsr}_{\text{Nh}2\text{o}} & := \frac{1}{3} \\
\text{Nco}_2\text{Nh}_2\text{o} & := -1 \\
\text{Nh}_2\text{Nh}_2\text{o} & := \frac{-7}{3}
\end{align*}
\]

\[
\begin{align*}
\text{Ngsr}_{\text{Nco}_2} & := \frac{-1}{3} \\
\text{Nh}_2\text{O}_\text{Nco}_2 & := -1 \\
\text{Nh}_2\text{Nco}_2 & := \frac{7}{3}
\end{align*}
\]

\[
\begin{align*}
\text{Ngsr}_{\text{Nh}2} & := \frac{-1}{7} \\
\text{Nh}_2\text{O}_{\text{Nh}2} & := \frac{-3}{7} \\
\text{Nco}_2\text{Nh}_2 & := \frac{3}{7}
\end{align*}
\]

Glycerol Multicomponent and Effective Diffusion Coefficients

\[
\text{DEN}_{\text{gsr}} := 1 - y_{\text{gsr}} \cdot (\text{Nh}_2\text{Ngsr} + \text{Nh}_2\text{O}_\text{Ngsr} + \text{Nco}_2\text{Ngsr})
\]

\[
\text{NUM}_{\text{gsr}} := \left( \frac{y_{\text{h}2}\text{o} - y_{\text{gsr}} \cdot \text{Nh}_2\text{O}_\text{Ngsr}}{\text{D}_{\text{gsr}_{\text{h}2}\text{o}}} \right) + \left( \frac{y_{\text{co}2} - y_{\text{gsr}} \cdot \text{Nco}_2\text{Ngsr}}{\text{D}_{\text{gsr}_{\text{co}2}}} \right) + \left( \frac{y_{\text{h}2} - y_{\text{gsr}} \cdot \text{Nh}_2\text{Ngsr}}{\text{D}_{\text{gsr}_{\text{h}2}}} \right)
\]

\[
\text{D}_{\text{gsr}_{\text{m}}} := \frac{10^{-4}}{\text{NUM}_{\text{gsr}}} \quad \text{D}_{\text{gsr}_{\text{m}}} = 9.331 \times 10^{-5} \text{ m/s}
\]

\[
\text{D}_{\text{gsr}} := \frac{1}{\left( \frac{1}{\text{D}_{\text{gsr}_{\text{m}}}} \right) + \left( \frac{1}{\text{DK}_{\text{gsr}}} \right)}
\]

\[
\text{D}_{\text{gsr}_{\text{eff}}} := \left( \frac{\epsilon}{\tau} \right) \cdot \text{D}_{\text{gsr}} = 1.146 \times 10^{-5} \text{ m/s}
\]
### H₂ Multicomponent and Effective Diffusion Coefficients

\[
\text{DEN}_h2 := 1 - yh2 \cdot (\text{Ngsr}_\text{Nh2} + \text{Nh2o}_\text{Nh2} + \text{Nco2}_\text{Nh2})
\]

\[
\text{NUM}_h2 := \left( \frac{yh2o - yh2\cdot Nh2o\cdot Nh2}{Dh2o\cdot Nh2} \right) + \left( \frac{yco2 - yh2\cdot Nco2\cdot Nh2}{Dco2\cdot Nh2} \right) + \left( \frac{ygsr - yh2\cdot Ngsr\cdot Nh2}{Dgsr\cdot Nh2} \right)
\]

\[
Dh2_m := \frac{10^{-4}}{\text{NUM}_h2} \text{DEN}_h2 \quad \text{Dh2}_m = 4.612 \times 10^{-4} \text{ m}^2/\text{s}
\]

\[
Dh2 := \frac{1}{\left( \frac{1}{Dh2_m} \right) + \left( \frac{1}{DK\cdot h2} \right)}
\]

\[
\text{Dh2\_eff} := \left( \frac{\epsilon}{\tau} \right) \cdot \text{Dh2} = 5.681 \times 10^{-5} \text{ m}^2/\text{s}
\]

### CO₂ Multicomponent and Effective Diffusion Coefficients

\[
\text{DEN\_co2} := 1 - yco2 \cdot (\text{Nh2\_Nco2} + \text{Nh2o\_Nco2} + \text{Ngsr\_Nco2})
\]

\[
\text{NUM\_co2} := \left( \frac{yh2o - yco2\cdot Nh2o\cdot Nco2}{Dh2o\cdot Nco2} \right) + \left( \frac{ygsr - yco2\cdot Ngsr\cdot Nco2}{Dgsr\cdot Nco2} \right) + \left( \frac{yco2 - yco2\cdot Nh2\cdot Nco2}{Dco2\cdot Nco2} \right)
\]

\[
Dco2_m := \frac{10^{-4}}{\text{NUM\_co2}} \text{DEN\_co2} \quad \text{Dco2}_m = 1.047 \times 10^{-4} \text{ m}^2/\text{s}
\]

\[
Dco2 := \frac{1}{\left( \frac{1}{Dco2_m} \right) + \left( \frac{1}{DK\cdot co2} \right)}
\]

\[
\text{Dco2\_eff} := \left( \frac{\epsilon}{\tau} \right) \cdot \text{Dco2} = 1.289 \times 10^{-5} \text{ m}^2/\text{s}
\]

### H₂O Multicomponent and Effective Diffusion Coefficients

\[
\text{DEN\_h2o} := 1 - yh2o \cdot (\text{Nh2\_Nh2o} + \text{Ngsr\_Nh2o} + \text{Nco2\_Nh2o})
\]

\[
\text{NUM\_h2o} := \left( \frac{yh2o - yh2o\cdot Ngsr\cdot Nh2o}{Dgsr\cdot h2o} \right) + \left( \frac{yco2 - yh2o\cdot Nco2\cdot Nh2o}{Dh2o\cdot Nco2} \right) + \left( \frac{y2 - yh2o\cdot Nh2\cdot Nh2o}{Dh2o\cdot Nh2} \right)
\]

\[
Dh2o_m := \frac{10^{-4}}{\text{NUM\_h2o}} \text{DEN\_h2o} \quad \text{Dh2o}_m = 4.3345 \times 10^{-4} \text{ m}^2/\text{s}
\]

\[
Dh2o := \frac{1}{\left( \frac{1}{Dh2o_m} \right) + \left( \frac{1}{DK\cdot h2o} \right)}
\]

\[
\text{Dh2o\_eff} := \left( \frac{\epsilon}{\tau} \right) \cdot \text{Dh2o} = 5.253 \times 10^{-5} \text{ m}^2/\text{s}
\]
Viscosity

From Perry's Handbook

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature</th>
<th>μP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>82.00 K</td>
<td>2.56</td>
</tr>
<tr>
<td>H2O</td>
<td>82.00 K</td>
<td>1.854</td>
</tr>
<tr>
<td>CO2</td>
<td>82.00 K</td>
<td>0.5</td>
</tr>
<tr>
<td>H2</td>
<td>82.00 K</td>
<td>0.5</td>
</tr>
</tbody>
</table>

From Yaw's Handbook

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature</th>
<th>μP</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>82.00 K</td>
<td>1.709610 (^{-8})</td>
</tr>
<tr>
<td>CO2</td>
<td>82.00 K</td>
<td>2.14810 (^{-6})</td>
</tr>
<tr>
<td>H2</td>
<td>82.00 K</td>
<td>0.68</td>
</tr>
<tr>
<td>CO2</td>
<td>82.00 K</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Dipole

μ1 := 2.56 \(\text{D}\) y1 := 0.1
μ2 := 1.854 y2 := 0.5
μ3 := 0 y3 := 0
μ4 := 0 y4 := 0

C1\(_{\text{h2o}}\) := 1.709610 \(^{-8}\)
C2\(_{\text{h2o}}\) := 1.114t
η2 := 10000000C1\(_{\text{h2o}}\) \(C_2\(_{\text{h2o}}\)\)
η2 := 303.668 μP

η3 := \(\frac{10000000C1\(_{\text{co2}}\) C2\(_{\text{co2}}\)}{1 + \left(\frac{C3\(_{\text{co2}}\)}{T}\right)}\)
η3 := 348.356 μP

η4 := \(\frac{10000000C1\(_{\text{h2}}\) C2\(_{\text{h}}\)}{1 + \left(\frac{C3\(_{\text{h2}}\) T}{C4\(_{\text{h2}}\) T^2}\right)}\)
η4 := 178.574 μP

η1 := C1\(_{\text{gsr}}\) + C2\(_{\text{gsr}}\)T + C3\(_{\text{gsr}}\)T^2
η1 := 196.202 μP

Tr12 := \(\frac{T}{(Tc1 \cdot Tc2)^{0.5}}\)
Tr13 := \(\frac{T}{(Tc1 \cdot Tc3)^{0.5}}\)
Tr14 := \(\frac{T}{(Tc1 \cdot Tc4)^{0.5}}\)
Tr23 := \(\frac{T}{(Tc2 \cdot Tc3)^{0.5}}\)
Tr24 := \(\frac{T}{(Tc2 \cdot Tc4)^{0.5}}\)
Tr34 := \(\frac{T}{(Tc3 \cdot Tc4)^{0.5}}\)

μr := \(\frac{52.46 \mu 1^2 \cdot Pc1}{Tc1^2}\)
μr2 := \(\frac{52.46 \mu 2^2 \cdot Pc2}{Tc2^2}\)
μr3 := 0
μr12 := (μr1 · μr2)^0.5
μr14 := 0
μr24 := 0
μr34 := 0
Fr1 := \( \frac{Tr1^{3.5} + (10 \mu_1)^7}{Tr1^{3.5}[1 + (10 \mu_1)^7]} \)  
Fr2 := \( \frac{Tr2^{3.5} + (10 \mu_2)^7}{Tr2^{3.5}[1 + (10 \mu_2)^7]} \)  
Fr3 := \( \frac{Tr3^{3.5}}{Tr3^{3.5}} \)  
Fr4 := 1

Fr12 := \( \frac{Tr12^{3.5} + (10 \mu_{12})^7}{Tr12^{3.5}[1 + (10 \mu_{12})^7]} \)  
Fr13 := \( \frac{Tr13^{3.5} + (10 \mu_{13})^7}{Tr13^{3.5}[1 + (10 \mu_{13})^7]} \)  
Fr14 := \( \frac{Tr14^{3.5} + (10 \mu_{14})^7}{Tr14^{3.5}[1 + (10 \mu_{14})^7]} \)

Fr23 := \( \frac{Tr23^{3.5} + (10 \mu_{23})^7}{Tr23^{3.5}[1 + (10 \mu_{23})^7]} \)  
Fr24 := \( \frac{Tr24^{3.5} + (10 \mu_{24})^7}{Tr24^{3.5}[1 + (10 \mu_{24})^7]} \)  
Fr34 := \( \frac{Tr34^{3.5} + (10 \mu_{34})^7}{Tr34^{3.5}[1 + (10 \mu_{34})^7]} \)

U1 := \( \frac{Fr1[1 + 0.36Tr1(Tr1 - 1)]}{(Tr1)^{0.5}} \)  
U2 := \( \frac{Fr2[1 + 0.36Tr2(Tr2 - 1)]}{(Tr2)^{0.5}} \)  
U3 := \( \frac{Fr3[1 + 0.36Tr3(Tr3 - 1)]}{(Tr3)^{0.5}} \)  
U4 := \( \frac{Fr4[1 + 0.36Tr4(Tr4 - 1)]}{(Tr4)^{0.5}} \)

C1 := \( \frac{M1^{0.25}}{(\eta1\cdot U1)^{0.5}} \)  
C2 := \( \frac{M2^{0.25}}{(\eta2\cdot U2)^{0.5}} \)  
C3 := \( \frac{M3^{0.25}}{(\eta3\cdot U3)^{0.5}} \)  
C4 := \( \frac{M4^{0.25}}{(\eta4\cdot U4)^{0.5}} \)

H12 := \( \left[ \frac{M1\cdot M2}{32(M1 + M2)^3} \right]^{0.5} (C1 + C2)^2 \left[ \frac{1}{[1 + 0.36Tr12(Tr12 - 1)]^6\cdot Fr12} \right] \)  
H13 := \( \left[ \frac{M1\cdot M3}{32(M1 + M3)^3} \right]^{0.5} (C1 + C3)^2 \left[ \frac{1}{[1 + 0.36Tr13(Tr13 - 1)]^6\cdot Fr13} \right] \)  
H14 := \( \left[ \frac{M1\cdot M4}{32(M1 + M4)^3} \right]^{0.5} (C1 + C4)^2 \left[ \frac{1}{[1 + 0.36Tr14(Tr14 - 1)]^6\cdot Fr14} \right] \)

55
\[ H_{23} := \left[ \frac{M_2M_3}{32(M_2 + M_3)^3} \right]^{0.5} (C_2 + C_3)^2 \left\{ \frac{1}{1 + 0.36Tr_{23}(Tr_{23} - 1)} \right\}^{6} 
\] 
\[ \frac{1}{(Tr_{23})^{0.5}} \]

\[ H_{24} := \left[ \frac{M_2M_4}{32(M_2 + M_4)^3} \right]^{0.5} (C_2 + C_4)^2 \left\{ \frac{1}{1 + 0.36Tr_{24}(Tr_{24} - 1)} \right\}^{6} 
\] 
\[ \frac{1}{(Tr_{24})^{0.5}} \]

\[ H_{34} := \left[ \frac{M_3M_4}{32(M_3 + M_4)^3} \right]^{0.5} (C_3 + C_4)^2 \left\{ \frac{1}{1 + 0.36Tr_{34}(Tr_{34} - 1)} \right\}^{6} 
\] 
\[ \frac{1}{(Tr_{34})^{0.5}} \]

\[ \eta_1 := \frac{y_1}{y_1 + \eta_1 \left[ y_2H_{12} \left( 3 + \left( \frac{2M_2}{M_1} \right) \right) + y_3H_{13} \left( 3 + \left( \frac{2M_3}{M_1} \right) \right) + y_4H_{14} \left( 3 + \left( \frac{2M_4}{M_1} \right) \right) \right]} \]

\[ K_1 := \frac{y_2}{y_2 + \eta_2 \left[ y_1H_{12} \left( 3 + \left( \frac{2M_1}{M_2} \right) \right) + y_3H_{23} \left( 3 + \left( \frac{2M_3}{M_2} \right) \right) + y_4H_{24} \left( 3 + \left( \frac{2M_4}{M_2} \right) \right) \right]} \]

\[ K_2 := \frac{y_3}{y_3 + \eta_3 \left[ y_1H_{13} \left( 3 + \left( \frac{2M_1}{M_3} \right) \right) + y_2H_{23} \left( 3 + \left( \frac{2M_2}{M_3} \right) \right) + y_4H_{34} \left( 3 + \left( \frac{2M_4}{M_3} \right) \right) \right]} \]

\[ K_3 := \frac{y_4}{y_4 + \eta_4 \left[ y_1H_{14} \left( 3 + \left( \frac{2M_1}{M_4} \right) \right) + y_2H_{24} \left( 3 + \left( \frac{2M_2}{M_4} \right) \right) + y_3H_{34} \left( 3 + \left( \frac{2M_3}{M_4} \right) \right) \right]} \]

\[ \eta_1 := K_1 \left[ 1 + H_1^2 \cdot K_2^2 + H_1^3 \cdot K_3^2 + H_1^4 \cdot K_4^2 + 2(H_1H_2K_1K_2) + 2(H_1H_2K_1K_4) + 2(H_1H_2K_3K_4) \right] \]

\[ \eta_2 := K_2 \left[ 1 + 2H_1K_1 + H_1^2 \cdot K_2^2 + H_2^3 \cdot K_3^2 + H_2^4 \cdot K_4^2 + 2(H_1H_2K_3K_4) + 2(H_1H_2K_1K_4) + 2(H_2H_3K_2K_4) \right] \]

\[ \eta_3 := K_3 \left[ 1 + 2(H_1K_1 + H_2K_2) + H_1^3 \cdot K_2^2 + H_2^3 \cdot K_2^2 + H_1^4 \cdot K_3^2 + 2(H_1H_2K_3K_4) + 2(H_2H_3K_1K_4) \right] \]

\[ \eta_4 := K_4 \left[ 1 + 2(H_1K_1 + H_2K_2 + H_3K_3) + H_1^3 \cdot K_2^2 + H_2^3 \cdot K_2^2 + H_3^3 \cdot K_3^2 + 2(H_1H_2K_1K_2) + 2(H_1H_3K_1K_4) + 2(H_2H_3K_2K_3) \right] \]

\[ \eta := \eta_1 + \eta_2 + \eta_3 + \eta_4 \]

\[ \eta := 273.939 \mu P \]
**Thermal Conductivity**

\[ T_1 := 82^\circ \text{C} \quad P := 1.0132 \text{ bar} \]

**Glycerol**

- \( T_c := 850 \text{ K} \)
- \( M_1 := 92.0938 \)
- \( P_c := 76 \)
- \( y_1 := 0.1 \)
- \( y_3 := 0 \)

**H}_2O**

- \( T_c := 647.1 \text{ K} \)
- \( M_2 := 18.01534 \)
- \( P_c := 220 \)
- \( y_2 := 0.9 \)
- \( y_4 := 0 \)

**CO}_2**

- \( T_c := 304.13 \text{ K} \)
- \( M_3 := 44.00995 \)
- \( P_c := 73.75 \)
- \( y_3 := 0 \)
- \( y_4 := 0 \)

**H}_2**

- \( T_c := 33.14 \text{ K} \)
- \( M_4 := 2.01594 \)
- \( P_c := 12.964 \)
- \( y_2 := 0.5 \)
- \( y_4 := 0 \)

**CO}_2 Thermal Conductivity: Perry’s Handbook**

\[
\lambda_3 := \frac{C_1_{co2} T^{C2_{co2}}}{1 + \left( \frac{C_3_{co2}}{T} \right) + \left( \frac{C_4_{co2}}{T^2} \right)} \quad \text{W/m.K}
\]

**H}_2 Thermal Conductivity: Perry’s Handbook**

\[
\lambda_4 := \frac{C_1_{h2} T^{C2_{h2}}}{1 + \left( \frac{C_3_{h2}}{T} \right)} \quad \text{W/m.K}
\]

**H}_2O Thermal Conductivity: Perry’s Handbook**

\[
\lambda_2 := C_1_{h2o} T^{C2_{h2}}
\]

**Glycerol Thermal Conductivity: Yaw’s Handbook**

\[
\lambda_1 := C_{1_{gsr}} + C_{2_{gsr}} T + C_{3_{gsr}} T^2 \quad \text{W/m.K}
\]

\[
\Gamma_1 := 210 \left( \frac{T_c - M_1^3}{P_c^4} \right)^{1/6} \quad \Gamma_2 := 210 \left( \frac{T_c - M_2^3}{P_c^4} \right)^{1/6} \quad \Gamma_3 := 210 \left( \frac{T_c - M_3^3}{P_c^4} \right)^{1/6} \quad \Gamma_4 := 210 \left( \frac{T_c - M_4^3}{P_c^4} \right)^{1/6}
\]
\[ \begin{align*}
\lambda_{12} & := \frac{\Gamma_2(\exp(0.0464T_{r1}) - \exp(-0.2412T_{r1}))}{\Gamma_1(\exp(0.0464T_{r2}) - \exp(-0.2412T_{r2}))} \\
\lambda_{13} & := \frac{\Gamma_3(\exp(0.0464T_{r1}) - \exp(-0.2412T_{r1}))}{\Gamma_1(\exp(0.0464T_{r3}) - \exp(-0.2412T_{r3}))} \\
\lambda_{14} & := \frac{\Gamma_4(\exp(0.0464T_{r1}) - \exp(-0.2412T_{r1}))}{\Gamma_1(\exp(0.0464T_{r4}) - \exp(-0.2412T_{r4}))} \\
\lambda_{23} & := \frac{\Gamma_3(\exp(0.0464T_{r2}) - \exp(-0.2412T_{r2}))}{\Gamma_2(\exp(0.0464T_{r3}) - \exp(-0.2412T_{r3}))} \\
\lambda_{24} & := \frac{\Gamma_4(\exp(0.0464T_{r2}) - \exp(-0.2412T_{r2}))}{\Gamma_2(\exp(0.0464T_{r4}) - \exp(-0.2412T_{r4}))} \\
\lambda_{34} & := \frac{\Gamma_4(\exp(0.0464T_{r3}) - \exp(-0.2412T_{r3}))}{\Gamma_3(\exp(0.0464T_{r4}) - \exp(-0.2412T_{r4}))}
\end{align*} \]

\[ \begin{align*}
A_{12} & := \left[ 1 + \lambda_{12}^{0.5} \left( \frac{M_1}{M_2} \right) \right]^{0.25^2} \\
A_{13} & := \left[ 1 + \lambda_{13}^{0.5} \left( \frac{M_1}{M_3} \right) \right]^{0.25^2} \\
A_{14} & := \left[ 1 + \lambda_{14}^{0.5} \left( \frac{M_1}{M_4} \right) \right]^{0.25^2} \\
A_{21} & := \left[ 1 + \lambda_{21}^{0.5} \left( \frac{M_2}{M_1} \right) \right]^{0.25^2} \\
A_{23} & := \left[ 1 + \lambda_{23}^{0.5} \left( \frac{M_2}{M_3} \right) \right]^{0.25^2} \\
A_{24} & := \left[ 1 + \lambda_{24}^{0.5} \left( \frac{M_2}{M_4} \right) \right]^{0.25^2} \\
A_{31} & := \left[ 1 + \lambda_{31}^{0.5} \left( \frac{M_3}{M_1} \right) \right]^{0.25^2} \\
A_{32} & := \left[ 1 + \lambda_{32}^{0.5} \left( \frac{M_3}{M_2} \right) \right]^{0.25^2} \\
A_{34} & := \left[ 1 + \lambda_{34}^{0.5} \left( \frac{M_3}{M_4} \right) \right]^{0.25^2} \\
A_{41} & := \left[ 1 + \lambda_{41}^{0.5} \left( \frac{M_4}{M_1} \right) \right]^{0.25^2} \\
A_{42} & := \left[ 1 + \lambda_{42}^{0.5} \left( \frac{M_4}{M_2} \right) \right]^{0.25^2} \\
A_{43} & := \left[ 1 + \lambda_{43}^{0.5} \left( \frac{M_4}{M_3} \right) \right]^{0.25^2}
\end{align*} \]
\[ \chi_m := \left( \frac{y_1 \cdot \chi_1}{y_1 + y_2 \cdot A_12 + y_3 \cdot A_13 + y_4 \cdot A_14} \right) + \left( \frac{y_2 \cdot \chi_2}{y_1 \cdot A_21 + y_2 + y_3 \cdot A_23 + y_4 \cdot A_24} \right) + \left( \frac{y_3 \cdot \chi_3}{y_1 \cdot A_31 + y_2 \cdot A_32 + y_3 + y_4 \cdot A_34} \right) + \left( \frac{y_4 \cdot \chi_4}{y_1 \cdot A_41 + y_2 \cdot A_42 + y_3 \cdot A_43 + y_4} \right) = 0.0716 \quad \text{W/m.K} \]

**Heat Capacity**

From Engineering Toolbox

\[ C_{p_{\text{h}_2}} := 14.7 \quad \text{kJ/kg.K} \]

\[ C_{p_{\text{fluent}_h2}} := 1000 \cdot C_{p_{\text{h}_2}} = 14740 \quad \text{J/kg.K} \]

From Perry's Handbook

\[ C_{1_{\text{co}_2}} := 0.293710^5 \quad C_{3_{\text{co}_2}} := 1.42810^3 \quad C_{5_{\text{co}_2}} := 588 \]

\[ C_{2_{\text{co}_2}} := 0.345410^5 \quad C_{4_{\text{co}_2}} := 0.26410^5 \]

\[ T := 823 \quad \text{K} \quad \text{MW}_{\text{co}_2} := 44.0099 \]

\[ C_{p_{\text{co}_2}} := C_{1_{\text{co}_2}} + C_{2_{\text{co}_2}} \left( \frac{C_{3_{\text{co}_2}}}{T} \right)^2 + C_{4_{\text{co}_2}} \left( \frac{C_{5_{\text{co}_2}}}{\cosh \left( \frac{C_{5_{\text{co}_2}}}{T} \right)} \right)^2 \]

\[ C_{p_{\text{co}_2}} = 5.156 \times 10^4 \quad \text{J/kg.K} \]

\[ C_{p_{\text{fluent}_{\text{co}_2}}} := \frac{C_{p_{\text{co}_2}}}{\text{MW}_{\text{co}_2}} = 1172 \quad \text{J/kg.K} \]

\[ C_{1_{\text{h}_2o}} := 0.3336310^5 \quad C_{3_{\text{h}_2o}} := 2.610510^3 \quad C_{5_{\text{h}_2o}} := 116 \]

\[ C_{2_{\text{h}_2o}} := 0.267910^5 \quad C_{4_{\text{h}_2o}} := 0.0889610^5 \quad \text{MW}_{\text{h}_2o} := 18.0153 \]

\[ C_{p_{\text{h}_2o}} := C_{1_{\text{h}_2o}} + C_{2_{\text{h}_2o}} \left( \frac{C_{3_{\text{h}_2o}}}{T} \right)^2 + C_{4_{\text{h}_2o}} \left( \frac{C_{5_{\text{h}_2o}}}{\cosh \left( \frac{C_{5_{\text{h}_2o}}}{T} \right)} \right)^2 \]
$C_{p_{\text{h}2o}} = 3.901 \times 10^4$ J/kmol.K

$C_{p_{\text{fluent h}2o}} := \frac{C_{p_{\text{h}2o}}}{MW_{\text{h}2o}} = 2165$ J/kg.K

From Yaw’s Handbook

$C_{1_{\text{g}sr}} := 9.65f$  
$C_{2_{\text{g}sr}} := 4.282610^{-1}$  
$MW_{\text{g}sr} := 92.0938$  

$C_{3_{\text{g}sr}} := -2.679710^{-4}$  
$C_{4_{\text{g}sr}} := 3.17910^{-8}$  
$C_{5_{\text{g}sr}} := 2.774510^{-11}$

$C_{p_{\text{g}sr}} := C_{1_{\text{g}sr}} + C_{2_{\text{g}sr}} T + C_{3_{\text{g}sr}} T^2 + C_{4_{\text{g}sr}} T^3 + C_{5_{\text{g}sr}} T^4$

$C_{p_{\text{g}sr}} = 211.06$ J/mol.K

$C_{p_{\text{fluent g}sr}} := \frac{1000 C_{p_{\text{g}sr}}}{MW_{\text{g}sr}} = 2292$ J/kg.K

$x_{\text{co}2} := 0$  
$x_{\text{h}2} := 0$  
$x_{\text{g}sr} := 0.36$

$x_{\text{h}2o} := 1 - (x_{\text{co}2} + x_{\text{h}2} + x_{\text{g}sr}) = 0.638$

$C_{p_{\text{mix}}} = x_{\text{co}2} C_{p_{\text{fluent co}2}} + x_{\text{h}2} C_{p_{\text{fluent h}2}} + x_{\text{g}sr} C_{p_{\text{fluent g}sr}} + x_{\text{h}2o} C_{p_{\text{fluent h}2o}}$

$C_{p_{\text{mix}}} = 2211$ J/kg.K
Appendix C: MATLAB Code

Profile file

clear all
global eps T dp r kprime kprime2 Ka Kb alpha Ca0 Fa0

R=8.314; %(m3 Pa)/(K mol)
Ka=5.6e-07; %Adsorption Constant, 1/Pa
Kb=4.3e-05;
eps=0.6; %net change in moles * yA0
rhocat=1947; %density of catalyst, kg/m3
P0=2*(101325); %(Pa
T=823; %K
Pi=3.14159;
visc=2.739e-05; %mixture viscosity, kg/(m.s)
yA0=0.1; %entering gsr mole fraction
yB0=0.9;
M_a=0.09209382;
M_b=0.01801534;
Sa=175100; %surface area of catalyst, m2/kg
i=0;

for Re = [100,200,300]
    for dp_inch = [1,1/2,1/3,1/4,1/5,1/6,1/7,1/8]
        i=i+1;

        dp=0.0254*dp_inch;
        D=5*0.0254; %2.76 to 6.3 inches

        kprime2=1.33e-11; %mol/(m2 s Pa^1.5)
        kprime=kprime2*Sa; %mol/(kg.s.Pa^1.5)

        N=D/dp;
        void=0.368*(1+(2/N)*((0.476/0.368)-1)); %Beavers et al. (1973)
        Ac=(Pi*D^2)/4;
        mdot=(Ac*visc*Re)/dp;
        G=mdot/Ac;
        MWavg0=yA0*M_a+yB0*M_b;
        rho0=(P0*MWavg0)/(R*T); %initial gas density
        xA0=yA0*(M_a/MWavg0); %initial mass fraction
        v0=mdot/rho0; %initial volumetric flow m3/s
        Fa0=(xA0*mdot)/M_a;
        Ca0=Fa0/v0;

        beta0=((G*(1:void))/((rho0*dp*void^3))*(((150*(1,void)*visc)/dp)+1.75*G); %Pa/m
        alpha=(2*beta0)/(Ac*rhocat*(1,void)*P0);

        Wend=(1:void)*Ac*12*rhocat;
        if alpha>0.005

            else
            ic=[0;1];
            wspan=[0 Wend];

[w,x]=ode45('GSR',wspan,ic);

f=(1+eps.*x(:,1))./x(:,2);
C_a=(Ca0.*x(:,2).*(1-x(:,1)))./(1+eps.*x(:,1));

z=w./(Ac*rhocat*(1-void));
P=P0.*x(:,2);
P_atm=P/101325;
X=x(:,1);
ConversionPercentage(i)=100*X(end);
Pf_atm(i)=P_atm(end);
Dp_inch(i)=dp_inch;
Reynolds(i)=Re;

output = [Reynolds' Dp_inch' ConversionPercentage' Pf_atm'];
output=output(max(output~=0,[],2),:);
end
end
end

Function file
function xdot=GSR(w,x)

global eps T dp R kprime Ka Kb alpha Ca0 Fa0

X=x(1);
y=x(2);

Ca=(Ca0*(1-X)*y)/(1+eps*X);
Cb=(Ca0*(9-3*X)*y)/(1+eps*X);

Pa=Ca*(R*T);
Pb=Cb*(R*T);

eta=(7.04492e-11)*dp^(-1.998617334); %effectiveness factor
raprime=eta*((kprime*Pa*(Pb^0.5)))/((1+Ka*Pa)*(1+((Kb*Pb)^0.5)))); %mol/kg.s

dxdw=raprime/Fa0;
dydw=-alpha*(1+eps*X)/(2*y);

xdot=[dxdw dydw]';
Appendix D: User Defined Functions

```c
#include "udf.h"
#include "mem.h"

/* gsr + 3h2o = 3co2 + 7h2 */
/* Gas constant in kJ/mol.K or m3.kPa/mol.K */
#define rgas 0.0083144
/* Solid density in kg/m3 */
#define rhos 1947
/* BET surface area in m^2/g */
#define BET 175.1
/* Diffusion Volumes, cm^3/mol */
#define vGSR 81.78
#define vh2 7.07
#define vco2 26.9
#define vh2o 12.7
/* Heats of reaction in J/kmol */
#define deltHdr -127670000 /* It's endothermic but negative because original code had opposite signs. */
/* Molecular weights in g/mol */
#define Mh2 2.01594
#define Mh2o 18.01534
#define Mco2 44.00995
#define Mgsr 92.09382

FILE *fout;

DEFINE_SOURCE(spe_uds0, cell, thread, dS, eqn) /*For Glycerol*/ { 
    real source;
    real kgsr, kh2o, rGSR, kRXN;
    real dPgsrdYgsr, drGSRdPgsr;
    real cell_temp, cell_press;
    real Yh2, Yco2, Yh2o, Ygsr, MWav, Ph2, Pco2, Ph2o, Pgsr;
    real p_operating;
    real kh2oPh2o, one_plus_kgsrPgsr;
    real alpha;

    p_operating = RP_Get_Real ("operating-pressure"); /* in Pa ????? */
    cell_temp = C_T(cell, thread);
    cell_press = p_operating/1000.0; /* in kPa */

    Ygsr = C_UDSI(cell, thread, 0);
    Yh2 = C_UDSI(cell, thread, 1);
    Yco2 = C_UDSI(cell, thread, 2);
    Yh2o = 1.0-Yh2-Yco2-Ygsr;

    MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);
    Ph2 = cell_press*Yh2*MWav/Mh2;
```
Pco2 = cell_press*Yco2*MWav/Mco2;
Ph2o = cell_press*Yh2o*MWav/Mh2o;
Pgsr = cell_press*Ygsr*MWav/Mgsr;

alpha = -1.0;
kgsr = 5.6e-04; /* kPa^-1 */
kh2o = 0.043; /* kPa^-1 */

kRXN = 0.001*1.33e-07; /* kPa^-1 */

rGSR = (kRXN*Pgsr*pow(Ph2o,0.5))/((1+kgsr*Pgsr)*(1+pow(kh2o,0.5)*pow(Ph2o,0.5))); /* kPa^-1 */

source = alpha*rhos*1000*rGSR*Mgsr*BET; /* 1000 is used to change units in rGSR to mol */

dPgsrdYgsr = cell_press*MWav/Mgsr*(1.0-Ygsr*MWav/Mgsr);

kh2oPh2o = kh2o*Ph2o;
one_plus_kgsrPgsr = 1+kgsr*Pgsr;

drGSRdPgsr = (kRXN*pow(Ph2o,0.5))/(pow(one_plus_kgsrPgsr,2)*(pow(kh2oPh2o,0.5)));

dS[eqn] = 1000*alpha*rhos*BET*Mgsr*drGSRdPgsr*dPgsrdYgsr;

return source;

DEFINE_SOURCE(spe_uds1, cell, thread, dS, eqn) /* For H2 */
{
    real source;
    real kgsr, kh2o, rGSR, kRXN;
    real dPh2dYh2, drGSRdPh2;
    real cell_temp, cell_press;
    real Yh2, Yco2, Yh2o, Ygsr, MWav, Ph2, Pco2, Ph2o, Pgsr;
    real p Operating;
    real alpha;

    p operating = RP_Get_Real("operating-pressure");
    cell temp = C_T(cell, thread);
    cell press = p operating/1000.0;

    Ygsr = C_UDSI(cell, thread, 0);
    Yh2 = C_UDSI(cell, thread, 1);
    Yco2 = C_UDSI(cell, thread, 2);
    Yh2o = 1.0-Yh2-Yco2-Ygsr;

    MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);

    Ph2 = cell_press*Yh2*MWav/Mh2;
    Pco2 = cell_press*Yco2*MWav/Mco2;
    Ph2o = cell_press*Yh2o*MWav/Mh2o;
    Pgsr = cell_press*Ygsr*MWav/Mgsr;

    alpha = 7.0;

    kgsr = 5.6e-04; /* kPa^-1 */
    kh2o = 0.043; /* kPa^-1 */
\[ k_{RXN} = 0.001 \times 1.33 \times 10^{-7}; /* \text{kmol m}^{-2} \text{s}^{-1} \text{kPa}^{-1.5} */ \]

\[ r_{GSR} = \frac{k_{RXN} \times \text{Pg} \times (\text{Ph}_{2o} \times 0.5)}{((1 + k_{gsr} \times \text{Pg})(1 + \text{power}(\text{kh}_{2o}, 0.5) \times \text{power}(\text{Ph}_{2o}, 0.5)))}; \]

\[ \text{source} = 1000 \times \alpha \times \rho \times r_{GSR} \times \text{M}_{\text{co}_{2}} \times \text{BET}; \]

\[ \text{dPh}_{2dYh}_{2} = \text{cell}_{press} \times \text{MW}_{\text{av}} \times \text{M}_{\text{h}_{2}} \times (1.0 - Y_{h_{2}} \times \text{MW}_{\text{av}} \times \text{M}_{\text{h}_{2}}); \]

\[ \text{dr}_{GSRdP}_{h2} = 0; \]

\[ \text{dS[eqn]} = 1000 \times \alpha \times \rho \times \text{BET} \times \text{M}_{\text{h}_{2}} \times \text{dr}_{GSRdP}_{h2} \times \text{dPh}_{2dYh}_{2}; \]

\[ \text{return source;} \]

DEFINE_SOURCE(spe_uds2, cell, thread, dS, eqn) /*For CO2*/
{
real source;
real kgsr, kh2o, rGSR, kRXN;
real dPco2dYco2, drGSRdPco2;
real cell_temp, cell_press;
real Yh2, Yco2, Yh2o, Ygsr, MWav, Ph2, Pco2, Ph2o, Pgsr;
real p_operating;
real alpha;

p_operating = RP_Get_Real(“operating-pressure”);
cell_temp = C_T(cell, thread);
cell_press = p_operating/1000.0;

Ygsr = C_UDSI(cell, thread, 0);
Yh2 = C_UDSI(cell, thread, 1);
Yco2 = C_UDSI(cell, thread, 2);
Yh2o = 1.0 - Yh2 - Yco2 - Ygsr;
MWav = 1.0/(Yco2/Mco2 + Yh2/Mh2 + Yh2o/Mh2o + Ygsr/Mgsr);
Ph2 = cell_press \times Yh2 \times MWav \times M_{h_{2}};
Pco2 = cell_press \times Yco2 \times MWav \times M_{co_{2}};
Ph2o = cell_press \times Yh2o \times MWav \times M_{h_{2}o};
Pgsr = cell_press \times Ygsr \times MWav \times M_{gsr};

alpha = 3.0;

kgsr = 5.6e-04; /* \text{kPa}^{-1} */
kh2o = 0.043; /* \text{kPa}^{-1} */

kRXN = 0.001 \times 1.33 \times 10^{-7}; /* \text{kmol m}^{-2} \text{s}^{-1} \text{kPa}^{-1.5} */

rGSR = \frac{k_{RXN} \times \text{Pg} \times \text{power}(\text{Ph}_{2o}, 0.5)}{((1 + k_{gsr} \times \text{Pg})(1 + \text{power}(\text{kh}_{2o}, 0.5) \times \text{power}(\text{Ph}_{2o}, 0.5)))};

\text{source} = 1000 \times \alpha \times \rho \times r_{GSR} \times \text{M}_{\text{co}_{2}} \times \text{BET};

\text{dPco2dYco2} = \text{cell}_{press} \times \text{MW}_{\text{av}} \times \text{M}_{\text{co}_{2}} \times (1.0 \times Y_{\text{co}_{2}} \times \text{MW}_{\text{av}} \times \text{M}_{\text{co}_{2}});

\text{dr}_{GSRdP}_{co2} = 0;

\text{dS[eqn]} = 1000 \times \alpha \times \rho \times \text{BET} \times \text{M}_{\text{h}_{2}} \times \text{dr}_{GSRdP}_{co2} \times \text{dPco2dYco2};

65
return source;
}

DEFINE_SOURCE(q_tdep, cell, thread, dS, eqn)
{
    real source;
    real kgsr, kh2o, rGSR, kRXN;
    real drGSRdt;
    real cell_temp, cell_press;
    real Yh2, Yco2, Yh2o, Ygsr, MWav, Ph2, Pco2, Ph2o, Pgsr;
    real p_operating;

    p_operating = RP_Get_Real("operating-pressure");
    cell_temp = C_T(cell, thread);
    cell_press = p_operating/1000.0; /* in kPa */

    Ygsr = C_UDSI(cell, thread, 0);
    Yh2 = C_UDSI(cell, thread, 1);
    Yco2 = C_UDSI(cell, thread, 2);
    Yh2o = 1.0 - Yh2 - Yco2 - Ygsr;

    MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);

    Ph2 = cell_press*Yh2*MWav/Mh2;
    Pco2 = cell_press*Yco2*MWav/Mco2;
    Ph2o = cell_press*Yh2o*MWav/Mh2o;
    Pgsr = cell_press*Ygsr*MWav/Mgsr;

    kgsr = 5.6e-04; /* kPa^-1 */
    kh2o = 0.043; /* kPa^-1 */

    kRXN = 0.001*1.33e-07; /* kmol m^-2 s^-1 kPa^-1.5 */

    rGSR = (kRXN*Pgsr*pow(Ph2o,0.5))/((1+kgsr*Pgsr)*(1+pow(kh2o,0.5)*pow(Ph2o,0.5)));

    source = 1000*rhos*BET*(delHr*rGSR); /* 1000 changes BET from g to kg in order to cancel units with rhos */
    /* delHr is in kmol so it cancels with kmol in rGSR */

    drGSRdt = 0;

    dS[eqn] = 1000*rhos*BET*(delHr*drGSRdt); /* 1000 changes BET from g to kg in order to cancel units with rhos */

    return source;
}

DEFINE_ADJUST(Yi_adjust, d)
{
    Thread *t;
    cell_t c;

    thread_loop_c(t, d)
    {

if (NNULLP(T_STORAGE_R(t,SV_P)))
    /* Test if it is fluid by seeing if pressure is available */
    {
        begin_c_loop(c,t)
            {  
            C_YI(c, t, 0) = C_UDSI(c, t, 0);
            C_YI(c, t, 1) = C_UDSI(c, t, 1);
            C_YI(c, t, 2) = C_UDSI(c, t, 2); 
        }
        end_c_loop(c,t)
    }

DEFINE_DIFFUSIVITY(uds0_diff,c,t,i) /*Effective Diffusivity for Glycerol*/
    {
        real diff;
        real cell_temp, p_operating, dens;
        real Ygsr, Yh2, Yco2, Yh2o, MWav, Mgsr_h2o, Mgsr_co2, Mgsr_h2;
        real Xgsr, Xh2, Xco2, Xh2o;
        real DK_gsr, Dgsr_m, Dgsr_h2o, Dgsr_h2, Dgsr, Dgsr_eff,Dgsr_co2;
        real rp;
        real temp_Mgsr;
        real porosity, tortuosity;
        real vGSR_H2O, vGSR_CO2, vGSR_H2;

        p_operating = RP_Get_Real("operating-pressure");
        cell_temp = C_T(c, t);
        Ygsr = C_UDSI(c, t, 0);
        Yh2 = C_UDSI(c, t, 1);
        Yco2 = C_UDSI(c, t, 2);
        Yh2o = 1.0 - Ygsr - Yh2 - Yco2;
        MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);
        dens = p_operating/rgas/cell_temp*MWav;
        dens = dens*1.0e-06; /* adjust density for wrong value of R */

        /*Mass Fractions to Mole Fractions*/
        Xgsr = Ygsr*(MWav/Mgsr);
        Xh2 = Yh2*(MWav/Mh2);
        Xco2 = Yco2*(MWav/Mco2);
        Xh2o = Yh2o*(MWav/Mh2o);

        Mgsr_h2o = (Mgsr+Mh2o)/(Mgsr*Mh2o);
        Mgsr_co2 = (Mgsr+Mco2)/(Mgsr*Mco2);
        Mgsr_h2 = (Mgsr+Mh2)/(Mgsr*Mh2);

        vGSR_H2O = pow(vGSR,0.3333)+pow(vh2o,0.3333);
        vGSR_CO2 = pow(vGSR, 0.3333)+pow(vco2,0.3333);
        vGSR_H2 = pow(vGSR, 0.3333)+pow(vh2,0.3333);

        /* Mutual Diffusivities, cm^2/s */
        Dgsr_h2o = (0.001*pow(cell_temp,1.75)*pow(Mgsr_h2o,0.5))/(p_operating*pow(vGSR_H2O,2));
Dgsr_co2 = (0.001*\(\text{pow}(\text{cell\_temp},1.75)\)*\(\text{pow}(\text{Mgsr\_co2},0.5)\))/(\(\text{p\_operating}\)*\(\text{pow}(v\text{GSR\_CO2},2)\));
Dgsr_h2 = (0.001*\(\text{pow}(\text{cell\_temp},1.75)\)*\(\text{pow}(\text{Mgsr\_h2},0.5)\))/(\(\text{p\_operating}\)*\(\text{pow}(v\text{GSR\_H2},2)\));

/*Equivalent Pore Radius, cm*/
rp = 2.581e-07;

/* Knudsen Diffusivity, cm^2/s */
temp_Mgsr = \text{cell\_temp}/\text{Mgsr};
DK_gsr = 9700*\text{rp}\*\text{pow}(\text{temp\_Mgsr},0.5);

/* Multicomponent Diffusivity, cm^2/s */
Dgsr_m = \((1+7*Xgsr)/(((Xh2+7*Xgsr)/Dgsr_h2)+((Xco2+3*Xgsr)/Dgsr_co2)+((Xh2o-3*Xgsr)/Dgsr_h2o))\);

/* Overall Diffusivity, cm^2/s */
Dgsr = 1/(\(\text{pow}(\text{Dgsr\_m},-1)\)+\(\text{pow}(\text{DK\_gsr},-1)\));

/* Effective Overall Diffusivity, m^2/s */
porosity = 0.44;
tortuosity = 3.54;
Dgsr_eff = 0.0001*(\text{porosity}/\text{tortuosity})*\text{Dgsr};
diff = Dgsr_eff*dens;
return diff;
}

DEFINE_DIFFUSIVITY(uds1_diff,c,t,i) /*Effective Diffusivity for H2*/
{
    real diff;
    real cell_temp, \text{p\_operating}, dens;
    real Ygsr, Yh2, Yco2, Yh2o, MWav, Mgsr_h2, Mh2_co2, Mh2_h2o;
    real Xgsr, Xh2, Xco2, Xh2o;
    real DK_h2, Dh2_m, Dgsr_h2, Dh2_h2o, Dh2_co2, Dh2, Dh2_eff;
    real rp;
    real temp_Mh2;
    real porosity, tortuosity;
    real vH2_GSR, vH2_H2O, vH2_CO2;

    \text{p\_operating} = \text{RP\_Get\_Real("operating\_pressure");}

    cell_temp = C_T(c, t);
    Ygsr = C_UDSI(c, t, 0);
    Yh2 = C_UDSI(c, t, 1);
    Yco2 = C_UDSI(c, t, 2);
    Yh2o = 1.0-Ygsr-Yh2-Yco2;
    MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);
dens = \text{p\_operating}/rgas/\text{cell\_temp}*MWav;
dens = dens*1.0e-06; /* adjust density for wrong value of R */

    /*Mass Fractions to Mole Fractions*/
    Xgsr = Ygsr*(MWav/Mgsr);
    Xh2 = Yh2*(MWav/Mh2);
    Xco2 = Yco2*(MWav/Mco2);
    Xh2o = Yh2o*(MWav/Mh2o);
Mgsr_h2 = (Mgsr+Mh2)/(Mgsr*Mh2);
Mh2_co2 = (Mh2+Mco2)/(Mh2*Mco2);
Mh2_h2o = (Mh2+Mh2o)/(Mh2*Mh2o);

vh2_GSR = pow(vh2,0.3333)+pow(vGSR,0.3333);
vh2_H2O = pow(vh2,0.3333)+pow(vh2o,0.3333);
vh2_CO2 = pow(vh2,0.3333)+pow(vco2,0.3333);

/* Mutual Diffusivities, cm^2/s */
Dgsr_h2 = (0.001*pow(cell_temp,1.75)*pow(Mgsr_h2,0.5))/(p_operating*pow(vH2_GSR,2));
Dh2_h2o = (0.001*pow(cell_temp,1.75)*pow(Mh2_h2o,0.5))/(p_operating*pow(vH2_H2O,2));
Dh2_co2 = (0.001*pow(cell_temp,1.75)*pow(Mh2_co2,0.5))/(p_operating*pow(vH2_CO2,2));

/* Equivalent Pore Radius, cm*/
rp = 2.581e-07;

/* Knudsen Diffusivity, cm^2/s */
temp_Mh2 = cell_temp/Mh2;
DK_h2 = 9700*rp*pow(temp_Mh2,0.5);

/* Multicomponent Diffusivity, cm^2/s */
Dh2_m = (1+(Xh2/7))/(((Xgsr+(Xh2/7))/Dgsr_h2)+((Xh2o+(3*Xh2/7))/Dh2_h2o)+((Xco2-(3*Xh2/7))/Dh2_co2));

/* Overall Diffusivity, cm^2/s */
Dh2 = 1/(pow(Dh2_m,-1)+pow(DK_h2,-1));

/* Effective Overall Diffusivity, m^2/s */
porosity = 0.44;
tortuosity = 3.54;
Dh2_eff = 0.0001*(porosity/tortuosity)*Dh2;
diff = Dh2_eff*dens;

return diff;
}

DEFINE_DIFFUSIVITY(uds2_diff,c,t,i) /*Effective Diffusivity for CO2*/
{
real diff;
real cell_temp, p_operating, dens;
real Ygsr, Yh2, Yco2, Yh2o, MWav, Mco2_gsr, Mco2_h2, Mco2_h2o;
real Xgsr, Xh2, Xco2, Xh2o;
real DK_co2, Dco2_m, Dco2_gsr, Dco2_h2, Dco2_h2o, Dco2, Dco2_eff;
real rp;
real temp_Mco2;
real porosity, tortuosity;
real vCO2_GSR, vCO2_H2, vCO2_H2O;

p_operating = RP_Get_Real ("operating-pressure");

cell_temp = C_T(c, t);

Ygsr = C_UDSI(c, t, 0);
Yh2 = C_UDSI(c, t, 1);
Yco2 = C_UDSI(c, t, 2);
Yh2o = 1.0-Ygsr-Yh2-Yco2;
MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);
dens = p_operating/rgas/cell_temp*MWav;
dens = dens*1.0e-06; /* adjust density for wrong value of R */

/*Mass Fractions to Mole Fractions*/
Xgsr = Ygsr*(MWav/Mgsr);
Xh2 = Yh2*(MWav/Mh2);
Xco2 = Yco2*(MWav/Mco2);
Xh2o = Yh2o*(MWav/Mh2o);

Mco2_gsr = (Mco2+Mgsr)/(Mco2*Mgsr);
Mco2_h2 = (Mco2+Mh2)/(Mco2*Mh2);
Mco2_h2o = (Mco2+Mh2o)/(Mco2*Mh2o);

vCO2_GSR = pow(vco2,0.3333)+pow(vGSR,0.3333);
vCO2_H2O = pow(vco2,0.3333)+pow(vh2o,0.3333);
vCO2_H2 = pow(vco2,0.3333)+pow(vh2,0.3333);

/* Mutual Diffusivities, cm^2/s */
Dco2_gsr = (0.001*pow(cell_temp,1.75)*pow(Mco2_gsr,0.5))/(p_operating*pow(vCO2_GSR,2));
Dco2_h2 = (0.001*pow(cell_temp,1.75)*pow(Mco2_h2,0.5))/(p_operating*pow(vCO2_H2,2));
Dco2_h2o = (0.001*pow(cell_temp,1.75)*pow(Mco2_h2o,0.5))/(p_operating*pow(vCO2_H2O,2));

/*Equivalent Pore Radius, cm*/
rp = 2.581e-07;

/* Knudsen Diffusivity, cm^2/s */
temp_Mco2 = cell_temp/Mco2;
DK_co2 = 9700*rp*pow(temp_Mco2,0.5);

/* Multicomponent Diffusivity, cm^2/s */
Dco2_m = (1-Xco2)/((Xgsr+(Xco2/3))/Dco2_gsr+((Xh2-(7*Xco2/3))/Dco2_h2)+((Xh2o+Xco2)/Dco2_h2o));

/* Overall Diffusivity, cm^2/s */
Dco2 = 1/(pow(Dco2_m,-1)+pow(DK_co2,-1));

/* Effective Overall Diffusivity, m^2/s */
porosity = 0.44;
tortuosity = 3.54;
Dco2_eff = 0.0001*(porosity/tortuosity)*Dco2;

diff = Dco2_eff*dens;
    return diff;
}

DEFINE_DIFFUSIVITY(uds0_fluid_diff,c,t,i) /* Multicomponent Diffusivity for Glycerol, m^2/s */
{
    real cell_temp, p_operating;
    real Ygsr, Yh2, Yco2, Yh2o, MWav, Mgsr_h2o, Mgsr_co2, Mgsr_h2;
    real Xgsr, Xh2, Xco2, Xh2o;
    real Dgsr_m, Dgsr_h2o, Dgsr_h2, Dgsr_co2;
    real vGSR_H2O, vGSR_CO2, vGSR_H2;
p_operating = RP_Get_Real("operating-pressure");

cell_temp = C_T(c, t);
Ygsr = C_UDSI(c, t, 0);
Yh2 = C_UDSI(c, t, 1);
Yco2 = C_UDSI(c, t, 2);
Yh2o = 1.0-Ygsr-Yh2-Yco2;
MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);

/*Mass Fractions to Mole Fractions*/
Xgsr = Ygsr*(MWav/Mgsr);
Xh2 = Yh2*(MWav/Mh2);
Xco2 = Yco2*(MWav/Mco2);
Xh2o = Yh2o*(MWav/Mh2o);

Mgsr_h2o = (Mgsr+Mh2o)/(Mgsr*Mh2o);
Mgsr_co2 = (Mgsr+Mco2)/(Mgsr*Mco2);
Mgsr_h2 = (Mgsr+Mh2)/(Mgsr*Mh2);

vGSR_H2O = pow(vGSR,0.3333)+pow(vh2o,0.3333);
vGSR_CO2 = pow(vGSR,0.3333)+pow(vco2,0.3333);
vGSR_H2 = pow(vGSR,0.3333)+pow(vh2,0.3333);

/* Mutual Diffusivities, cm^2/s */
Dgsr_h2o = (0.001*pow(cell_temp,1.75)*pow(Mgsr_h2o,0.5))/(p_operating*pow(vGSR_H2O,2));
Dgsr_co2 = (0.001*pow(cell_temp,1.75)*pow(Mgsr_co2,0.5))/(p_operating*pow(vGSR_CO2,2));
Dgsr_h2 = (0.001*pow(cell_temp,1.75)*pow(Mgsr_h2,0.5))/(p_operating*pow(vGSR_H2,2));

/* Multicomponent Diffusivity, cm^2/s */
Dgsr_m = (1+7*Xgsr)/(((Xh2+7*Xgsr)/Dgsr_h2)+((Xco2+3*Xgsr)/Dgsr_co2)+((Xh2o-3*Xgsr)/Dgsr_h2o));

return C_R(c,t) * 0.0001 * Dgsr_m + C_MU_T(c,t)/0.7;
}

DEFINE_DIFFUSIVITY(uds1_fluid_diff,c,t,i) /* Multicomponent Diffusivity for H2, m^2/s */ {
real cell_temp, p_operating;
real Ygsr, Yh2, Yco2, Yh2o, MWav, Mgsr_h2, Mh2_co2, Mh2_h2o;
real Xgsr, Xh2, Xco2, Xh2o;
real Dh2_m, Dgsr_h2, Dh2_h2o, Dh2_co2;
real vH2_GSR, vH2_H2O, vH2_CO2;

p_operating = RP_Get_Real("operating-pressure");

cell_temp = C_T(c, t);
Ygsr = C_UDSI(c, t, 0);
Yh2 = C_UDSI(c, t, 1);
Yco2 = C_UDSI(c, t, 2);
Yh2o = 1.0-Ygsr-Yh2-Yco2;
MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);

/*Mass Fractions to Mole Fractions*/
Xgsr = Ygsr*(MWav/Mgsr);
Xh2 = Yh2*(MWav/Mh2);
Xco2 = Yco2*(MWav/Mco2);
Xh2o = Yh2o*(MWav/Mh2o);

Mgsr_h2 = (Mgsr+Mh2)/(Mgsr*Mh2);
Mh2_co2 = (Mh2+Mco2)/(Mh2*Mco2);
Mh2_h2o = (Mh2+Mh2o)/(Mh2*Mh2o);

vH2_GSR = pow(vh2,0.3333)+pow(vGSR,0.3333);
vH2_H2O = pow(vh2,0.3333)+pow(vh2o,0.3333);
vH2_CO2 = pow(vh2,0.3333)+pow(vco2,0.3333);

/* Mutual Diffusivities, cm^2/s */
Dgsr_h2 = (0.001*pow(cell_temp,1.75)*pow(Mgsr_h2,0.5))/(p_operating*pow(vH2_GSR,2));
Dh2_h2o = (0.001*pow(cell_temp,1.75)*pow(Mh2_h2o,0.5))/(p_operating*pow(vH2_H2O,2));
Dh2_co2 = (0.001*pow(cell_temp,1.75)*pow(Mh2_co2,0.5))/(p_operating*pow(vH2_CO2,2));

/* Multicomponent Diffusivity, cm^2/s */
Dh2_m = (1+(Xh2/7))/(((Xgsr+(Xh2/7))/Dgsr_h2)+((Xh2o+(3*Xh2/7))/Dh2_h2o)+((Xco2-(3*Xh2/7))/Dh2_co2));

return C_R(c,t) * 0.0001 * Dh2_m + C_MU_T(c,t)/0.7;
}

DEFINE_DIFFUSIVITY(uds2_fluid_diff,c,t,i) /* Multicomponent Diffusivity for CO2, m^2/s */
{
    real cell_temp, p_operating;
    real Ygsr, Yh2, Yco2, Yh2o, MWav, Mco2_gsr, Mco2_h2, Mco2_h2o;
    real Xgsr, Xh2, Xco2, Xh2o;
    real Dco2_m, Dco2_gsr, Dco2_h2, Dco2_h2o;
    real vCO2_GSR, vCO2_H2, vCO2_H2O;

    p_operating = RP_Get_Real ("operating-pressure");

    cell_temp = C_T(c, t);
    Ygsr = C_UDSI(c, t, 0);
    Yh2 = C_UDSI(c, t, 1);
    Yco2 = C_UDSI(c, t, 2);
    Yh2o = 1.0-Ygsr-Yh2-Yco2;
    MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);

    /*Mass Fractions to Mole Fractions*/
    Xgsr = Ygsr*(MWav/Mgsr);
    Xh2 = Yh2*(MWav/Mh2);
    Xco2 = Yco2*(MWav/Mco2);
    Xh2o = Yh2o*(MWav/Mh2o);

    Mco2_gsr = (Mco2+Mgsr)/(Mco2*Mgsr);
    Mco2_h2 = (Mco2+Mh2)/(Mco2*Mh2);
    Mco2_h2o = (Mco2+Mh2o)/(Mco2*Mh2o);

    vCO2_GSR = pow(vco2,0.3333)+pow(vGSR,0.3333);
    vCO2_H2O = pow(vco2,0.3333)+pow(vh2o,0.3333);
    vCO2_H2 = pow(vco2,0.3333)+pow(vh2,0.3333);
/* Mutual Diffusivities, cm^2/s */
Dco2_gsr = (0.001*pow(cell_temp,1.75)*pow(Mco2_gsr,0.5))/(p_operating*pow(vCO2_GSR,2));
Dco2_h2 = (0.001*pow(cell_temp,1.75)*pow(Mco2_h2,0.5))/(p_operating*pow(vCO2_H2,2));
Dco2_h2o = (0.001*pow(cell_temp,1.75)*pow(Mco2_h2o,0.5))/(p_operating*pow(vCO2_H2O,2));

/* Multicomponent Diffusivity, cm^2/s */
Dco2_m = (1-Xco2)/(((Xgsr+(Xco2/3))/Dco2_gsr)+((Xh2-(7*Xco2/3))/Dco2_h2)+((Xh2o+Xco2)/Dco2_h2o));

return C_R(c,t) * 0.0001 * Dco2_m + C_MU_T(c,t)/0.7;

DEFINE_PROFILE(coupled_uds_0, t, i)
{
    Thread *tc0, *tc1;
    cell_t c0,c1;
    face_t f;

    real A[ND_ND], x0[ND_ND], x1[ND_ND], C1COORD[ND_ND], C0COORD[ND_ND], FCOORD[ND_ND];
    real e_x0[ND_ND], e_x1[ND_ND];
    real uds_b, diff0, diff1;
    real h0, h1, A_by_ex0, A_by_ex1;
    real dx0, dx1;

    begin_f_loop(f, t)
    {
        F_AREA(A,f,t);
        c0 = F_C0(f, t);
        c1 = F_C1(f, t);
        tc0 = THREAD_T0(t);
        tc1 = THREAD_T1(t);
        C_CENTROID(C0_COORD, c0, tc0);
        C_CENTROID(C1_COORD, c1, tc1);
        F_CENTROID(FCOORD, f, t);
        NV_VV(x0, =, FCOORD, -, C0COORD);
        dx0 = NV_MAG(x0);
        NV_VV(x1, =, FCOORD, -, C1COORD);
        dx1 = NV_MAG(x1);
        NV_VS(e_x0, =, x0, /, dx0);
        NV_VS(e_x1, =, x1, /, dx1);
        A_by_ex0 = NV_DOT(A,A)/NV_DOT(e_x0,A);
        A_by_ex1 = NV_DOT(A,A)/NV_DOT(e_x1,A);
        diff0 = C_UDSI_DIFF(c0,tc0,0);
        diff1 = C_UDSI_DIFF(c1,tc1,0);
        h0 = diff0/dx0*A_by_ex0;
        h1 = -diff1/dx1*A_by_ex1;
        uds_b = (h0*C_UDSI(c0,tc0,0) + h1*C_UDSI(c1,tc1,0))/(h0+h1);
        F_PROFILE(f,t,i) = uds_b;
    }
    end_f_loop(f, t)
}

DEFINE_PROFILE(coupled_uds_1, t, i)
{
    Thread *tc0, *tc1;
    cell_t c0,c1;
    face_t f;
real A[ND_ND], x0[ND_ND], x1[ND_ND], C1_COORD[ND_ND], C0COORD[ND_ND], F_COORD[ND_ND];
real e_x0[ND_ND], e_x1[ND_ND];
real uds_b, diff0, diff1;
real h0, h1, A_by_ex0, A_by_ex1;
real dx0, dx1;

begin_f_loop(f, t)
{
    F_AREA(A,f,t);
c0 = F_C0(f, t);
c1 = F_C1(f, t);
tc0 = THREAD_T0(t);
tc1 = THREAD_T1(t);
C_CENTROID(C0COORD, c0, tc0);
C_CENTROID(C1COORD, c1, tc1);
F_CENTROID(FCOORD, f, t);
NV_VV(x0, =, FCOORD, - , C0COORD);
dx0 = NV_MAG(x0);
NV_VV(x1, =, FCOORD, - , C1COORD);
dx1 = NV_MAG(x1);
NV_VS(e_x0, =, x0, /, dx0);
NV_VS(e_x1, =, x1, /, dx1);
A_by_ex0 = NV_DOT(A,A)/NV_DOT(e_x0,A);
A_by_ex1 = NV_DOT(A,A)/NV_DOT(e_x1,A);
diff0 = C_UDSI_DIFF(c0,tc0,1);
diff1 = C_UDSI_DIFF(c1,tc1,1);
h0 = diff0/dx0*A_by_ex0;
h1 = -diff1/dx1*A_by_ex1;
uds_b = (h0*C_UDSI(c0,tc0,1) + h1*C_UDSI(c1,tc1,1))/(h0+h1);
F_PROFILE(f,t,i) = uds_b;
}
end_f_loop(f, t)

DEFINE_PROFILE(coupled_uds_2, t, i)
{
    Thread *tc0, *tc1;
    cell_t c0,c1;
    face_t f;

    real A[ND_ND], x0[ND_ND], x1[ND_ND], C1_COORD[ND_ND], C0COORD[ND_ND], F_COORD[ND_ND];
    real e_x0[ND_ND], e_x1[ND_ND];
    real uds_b, diff0, diff1;
    real h0, h1, A_by_ex0, A_by_ex1;
    real dx0, dx1;

    begin_f_loop(f, t)
    {
        F_AREA(A,f,t);
c0 = F_C0(f, t);
c1 = F_C1(f, t);
tc0 = THREAD_T0(t);
tc1 = THREAD_T1(t);
C_CENTROID(C0COORD, c0, tc0);
C_CENTROID(C1COORD, c1, tc1);
F_CENTROID(FCOORD, f, t);
NV_VV(x0, =, FCOORD, - , C0COORD);
dx0 = NV_MAG(x0);
NV_VV(x1, =, FCOORD, -, C1COORD);
dx1 = NV_MAG(x1);
NV_VS(e_x0, =, x0, /, dx0);
NV_VS(e_x1, =, x1, /, dx1);
A_by_ex0 = NV_DOT(A,A)/NV_DOT(e_x0,A);
A_by_ex1 = NV_DOT(A,A)/NV_DOT(e_x1,A);
diff0 = C_UDSI_DIF(c0,tc0,2);
diff1 = C_UDSI_DIFF(c1,tc1,2);
h0 = diff0/dx0*A_by_ex0;
h1 = -diff1/dx1*A_by_ex1;
uds_b = (h0*C_UDSI(c0,tc0,2) + h1*C_UDSI(c1,tc1,2))/(h0+h1);
F_PROFILE(f,t,i) = uds_b;
}
end_f_loop(f, t)

/* START OF DEFINE-ON-DEMAND SUBROUTINES
###############################################################################
####*/

DEFINE_ON_DEMAND(reaction_rates_particles)
{
    Domain *d;
    Thread *thread;
    cell_t cell;

    int ID, uds_i;
    real R1sink, psink1, csink1;
    real kgsr, kh2o, rGSR, kRXN;
    real cell_vol, cell_temp, cell_press, p_operating;
    real Yh2, Yco2, Yh2o, Ygsr, MWav, Ph2, Pco2, Ph2o, Pgsr;
    real uds_tot[3], uds_part[3], uds_cell[3];

d = Get_Domain(1);
R1sink = 0;

for (uds_i = 0; uds_i <= 2; ++uds_i)
{
    uds_tot[uds_i] = 0;
}

fout = fopen("part_rxns", "w");

for (ID = 2; ID <= 16; ++ID)
{
    thread = Lookup_Thread(d, ID);
    psink1 = 0;

    for (uds_i = 0; uds_i <= 2; ++uds_i)
    {
        uds_part[uds_i] = 0;
    }
}
begin_c_loop(cell, thread)
{
    cell_vol = C_VOLUME(cell, thread);
    cell_temp = C_T(cell, thread);
    p_operating = RP_Get_Real("operating-pressure");
    cell_press = p_operating/1000.0;

    Ygsr = C_UDSI(cell, thread, 0);
    Yh2 = C_UDSI(cell, thread, 1);
    Yco2 = C_UDSI(cell, thread, 2);
    Yh2o = 1.0-Yh2-Yco2-Ygsr;
    MWav = 1.0/(Yco2/Mco2+Yh2/Mh2+Yh2o/Mh2o+Ygsr/Mgsr);
    Ph2 = cell_press*Yh2*MWav/Mh2;
    Pco2 = cell_press*Yco2*MWav/Mco2;
    Ph2o = cell_press*Yh2o*MWav/Mh2o;
    Pgsr = cell_press*Ygsr*MWav/Mgsr;

    if (cell_temp <= 550)
    {
        csink1 = 0.0;
        for (uds_i = 0; uds_i <= 2; ++uds_i)
        {
            uds_cell[uds_i] = 0;
        }
    }
    else /*HERE*/
    {
        kgsr = 5.6e-04; /* kPa^-1 */
        kh2o = 0.043; /* kPa^-1 */
        kRXN = 0.001*1.33e-07; /*kmol m^-2 s^-1 kPa^-1.5*/
        rGSR = (kRXN*Pgsr*pow(Ph2o,0.5))/((1+kgsr*Pgsr)*(1+pow(kh2o,0.5)*pow(Ph2o,0.5))); /*kmol / (m^2 * s) */
        csink1 = cell_vol*rhos*rGSR*BET*1000; /* kmol/s */
        uds_cell[0] = cell_vol*rhos*(-rGSR)*BET*1000*Mgsr; /* kg/s */
        uds_cell[1] = cell_vol*rhos*(7*rGSR)*BET*1000*Mh2;
        uds_cell[2] = cell_vol*rhos*(3*rGSR)*BET*1000*Mco2;
        psink1 = csink1 + psink1;
        for (uds_i = 0; uds_i <= 2; ++uds_i)
        {
            uds_part[uds_i] = uds_part[uds_i] + uds_cell[uds_i];
        }
        fprintf(fout,"%d %g %g %g %g %g %g %g %g\n", ID, cell_temp, cell_press, csink1, uds_cell[0], uds_cell[1], uds_cell[2]);
    }
}
end_c_loop(f,t)

fprintf(fout, "\n");
printf("\n");
printf("Particle %d   Reaction (kmol/s): %g \n", ID, psink1); /*from csink1*/
printf("Particle %d   GSR consumption (kg/s): %g \n", ID, uds_part[0]); /* from uds_cell[0] */
printf("Particle %d   H2 production (kg/s): %g \n", ID, uds_part[1]);
printf("Particle %d   CO2 production (kg/s): %g \n", ID, uds_part[2]);
R1sink = R1sink + psink1;

for (uds_i = 0; uds_i <= 2; ++uds_i)
{
    uds_tot[uds_i] = uds_tot[uds_i] + uds_part[uds_i];
}
printf("\n");
printf("Total reaction (kmol/s): %g \n", R1sink);
printf("Total GSR consumption (kg/s): %g \n", uds_tot[0]);
printf("Total H2 production (kg/s): %g \n", uds_tot[1]);
printf("Total CO2 production (kg/s): %g \n", uds_tot[2]);
fclose(fout);

DEFINE_ON_DEMAND(solid_species_surface_flow)
{
    Domain *d;
    Thread *t, *tc0, *tc1;
    cell_t c0,c1;
    face_t f;

    real A[ND_ND], x0[ND_ND], x1[ND_ND], es0[ND_ND], es1[ND_ND], xf[ND_ND];
    real grad_0[ND_ND], grad_1[ND_ND];
    real pgrad, h0, h1;
    real mag, area, ds0, ds1, A_by_es0, A_by_es1;
    real dx0, dx1, e_x0[ND_ND], e_x1[ND_ND];
    int wall_id, uds_i;
    real uds_0, uds_1, diff0, diff1;
    real uds_face_flow[3], uds_flow[3], uds_flow_tot[3], uds_flux[3], MW[3];

    d = Get_Domain(1); /*Get the domain ID*/
    MW[0] = Mgsr;
    MW[1] = Mh2;
    MW[2] = Mco2;

    for (uds_i = 0; uds_i <= 2; ++uds_i)
    {
        uds_flow_tot[uds_i] = 0;
    }

    fout = fopen("species_surface_flows", "w");

    for (wall_id = 24; wall_id <= 36; wall_id+=2)
    {
        /* Get the thread id of that surface*/
        t = Lookup_Thread(d,wall_id);

        for (uds_i = 0; uds_i <= 2; ++uds_i)
        {
            uds_flow[uds_i] = 0;
        }
area = 0;

/* Loop over all surface faces*/
begin_f_loop(f,t)
{
    F_AREA(A,f,t);       /*Get the area vector*/
    mag = NV_MAG(A);
    c0 = F_C0(f,t);      /*Get the adjacent C0 cell*/
    c1 = F_C1(f,t);      /*Get the adjacent C1 cell*/
    tc0 = THREAD_T0(t);
    tc1 = THREAD_T1(t);
    C_CENTROID(x0,c0,tc0);
    C_CENTROID(x1,c1,tc1);
    F_CENTROID(xf, f,t);
    NV_VV(es0, =, xf,-,x0);
    NV_VV(es1, =, xf,-,x1);
    ds0 = NV_MAG(es0);
    ds1 = NV_MAG(es1);
    NV_S(es0, /=,ds0);
    NV_S(es1, /=,ds1);
    A_by_es0 = NV_DOT(A,A)/NV_DOT(es0,A);
    A_by_es1 = NV_DOT(A,A)/NV_DOT(es1,A);
    for (uds_i = 0;  uds_i <= 2;  ++uds_i)
    {
        diff0 = C_UDSI_DIFF(c0,tc0,uds_i);
        diff1 = C_UDSI_DIFF(c1,tc1,uds_i);
        h0 = diff0/ds0*A_by_es0;
        h1 = -diff1/ds1*A_by_es1;
        uds_0 = C_UDSI(c0,tc0,uds_i);
        uds_1 = C_UDSI(c1,tc1,uds_i);
        pgrad = (uds_1-uds_0)*h0*h1/(h0+h1);
        uds_face_flow[uds_i] = (pgrad)/MW[uds_i];
        uds_flow[uds_i] = uds_face_flow[uds_i] / area;
        uds_flow_tot[uds_i] = uds_flow_tot[uds_i] + uds_flow[uds_i];
    }
    area = area + mag;
    fprintf(fout, "%d %g %g %g %g %g %g %g\n", wall_id, xf[0], xf[1], xf[2], mag,
            uds_face_flow[0], uds_face_flow[1], uds_face_flow[2]);
}
end_f_loop(f,t)

for (uds_i = 0;  uds_i <= 2;  ++uds_i)
{
    uds_flux[uds_i] = uds_flow[uds_i]/area;
    uds_flow_tot[uds_i] = uds_flow_tot[uds_i] + uds_flow[uds_i];
}
printf("\n");
printf("Wall ID: %d GSR flux (kmol/m2-s): %g GSR flow (kmol/s): %g\n", wall_id,
       uds_flux[0], uds_flow[0]);
printf("Wall ID: %d H2 flux (kmol/m2-s): %g H2 flow (kmol/s): %g\n", wall_id,
       uds_flux[1], uds_flow[1]);
printf("Wall ID: %d CO2 flux (kmol/m2-s): %g CO2 flow (kmol/s): %g\n", wall_id,
       uds_flux[2], uds_flow[2]);
}
for (wall_id = 38;  wall_id <= 44;  ++wall_id)
{
    /* Get the thread id of that surface*/

t = Lookup_Thread(d,wall_id);

for (uds_i = 0; uds_i <= 2; ++uds_i)
{
    uds_flow[uds_i] = 0;
}

area = 0;

/* Loop over all surface faces*/
begin_f_loop(f,t)
{
    F_AREA(A,f,t);       /*Get the area vector*/
    mag = NV_MAG(A);
    c0 = F_C0(f,t);      /*Get the adjacent C0 cell*/
    c1 = F_C1(f,t);      /*Get the adjacent C1 cell*/
    tc0 = THREAD_T0(t);
    tc1 = THREAD_T1(t);
    C_CENTROID(x0,c0,tc0);
    C_CENTROID(x1,c1,tc1);
    F_CENTROID(xf, f,t);
    NV_VV(es0, =, xf, -x0);
    NV_VV(es1, =, xf, -x1);
    ds0 = NV_MAG(es0);
    ds1 = NV_MAG(es1);
    NV_S(es0, /=, ds0);
    NV_S(es1, /=, ds1);
    A_by_es0 = NV_DOT(A,A)/NV_DOT(es0,A);
    A_by_es1 = NV_DOT(A,A)/NV_DOT(es1,A);
    for (uds_i = 0; uds_i <= 2; ++uds_i)
    {
        diff0 = C_UDSI_DIFF(c0,tc0,uds_i);
        diff1 = C_UDSI_DIFF(c1,tc1,uds_i);
        h0 = diff0/ds0*A_by_es0;
        h1 = -diff1/ds1*A_by_es1;
        uds_0 = C_UDSI(c0,tc0,uds_i);
        uds_1 = C_UDSI(c1,tc1,uds_i);
        pgrad = (uds_1-uds_0)*h0*h1/(h0+h1);
        uds_face_flow[uds_i] = uds_flow[uds_i] + uds_face_flow[uds_i];
    }
    area = area + mag;
    fprintf(fout, "%d %g %g %g %g %g %g %g
", wall_id, xf[0], xf[1], xf[2], mag, uds_face_flow[0], uds_face_flow[1], uds_face_flow[2]);
}
end_f_loop(f,t)

for (uds_i = 0; uds_i <= 2; ++uds_i)
{
    uds_flux[uds_i] = uds_flow[uds_i]/area;
    uds_flow_tot[uds_i] = uds_flow_tot[uds_i] + uds_flow[uds_i];
}
printf("\n");
printf("Wall ID: %d    GSR flux (kmol/m^2-s): %g    GSR flow (kmol/s): %g\n", wall_id, uds_flux[0], uds_flow[0]);
printf("Wall ID: %d    H2 flux (kmol/m^2-s): %g    H2 flow (kmol/s): %g\n", wall_id, uds_flux[1], uds_flow[1]);
printf("Wall ID: %d    CO2 flux (kmol/m2-s): %g    CO2 flow (kmol/s): %g\n", wall_id, uds_flux[2], uds_flow[2]);
}
for (wall_id =48; wall_id <= 48; ++wall_id) /*part 2-7*/
/*
 */
{
  /* Get the thread id of that surface*/
  t = Lookup_Thread(d,wall_id);

  for (uds_i = 0; uds_i <= 2; ++uds_i)
  {
    uds_flow[uds_i] = 0;
  }
  area = 0;

  /* Loop over all surface faces*/
  begin_f_loop(f,t)
  {
    F_AREA(A,f,t);     /*Get the area vector*/
    mag = NV_MAG(A);
    c0 = F_C0(f,t);     /*Get the adjacent C0 cell*/
    c1 = F_C1(f,t);     /*Get the adjacent C1 cell*/
    tc0 = THREAD_T0(t);
    tc1 = THREAD_T1(t);
    C_CENTROID(x0,c0,tc0);
    C_CENTROID(x1,c1,tc1);
    F_CENTROID(xf,f,t);
    NV_VV(es0, =, xf,-,x0);
    NV_VV(es1, =, xf,-,x1);
    ds0 = NV_MAG(es0);
    ds1 = NV_MAG(es1);
    NV_S(es0,/=,ds0);
    NV_S(es1,/=,ds1);
    A_by_es0 = NV_DOT(A,A)/NV_DOT(es0,A);
    A_by_es1 = NV_DOT(A,A)/NV_DOT(es1,A);
    for (uds_i = 0; uds_i <= 2; ++uds_i)
    {
      diff0 = C_UDSI_DIFF(c0,tc0,uds_i);
      diff1 = C_UDSI_DIFF(c1,tc1,uds_i);
      h0 = diff0/ds0*A_by_es0;
      h1 = -diff1/ds1*A_by_es1;
      uds_0 = C_UDSI(c0,tc0,uds_i);
      uds_1 = C_UDSI(c1,tc1,uds_i);
      pgrad = (uds_1-uds_0)*h0*h1/(h0+h1);
      uds_face_flow[uds_i] = (pgrad)/MW[uds_i];
      uds_flow[uds_i] = uds_flow[uds_i] + uds_face_flow[uds_i];
    }
    area = area + mag;
    fprintf(fout, "%d %g %g %g %g %g %g %g %g %g
", wall_id, xf[0], xf[1], xf[2], mag, uds_face_flow[0], uds_face_flow[1], uds_face_flow[2]);
  }
  end_f_loop(f,t)

  for (uds_i = 0; uds_i <= 2; ++uds_i)
{  
    uds_flux[uds_i] = uds_flow[uds_i]/area;
    uds_flow_tot[uds_i] = uds_flow_tot[uds_i] + uds_flow[uds_i];
}
printf("\n");
printf("Wall ID: %d    GSR flux (kmol/m2-s): %g    GSR flow (kmol/s): %g\n", wall_id,
    uds_flux[0], uds_flow[0]);
printf("Wall ID: %d    H2 flux (kmol/m2-s): %g    H2 flow (kmol/s): %g\n", wall_id,
    uds_flux[1], uds_flow[1]);
printf("Wall ID: %d    CO2 flux (kmol/m2-s): %g    CO2 flow (kmol/s): %g\n", wall_id,
    uds_flux[2], uds_flow[2]);
}
printf("\n");
printf("Total particle GSR flow (kmol/s): %g\n", uds_flow_tot[0]);
printf("Total particle H2 flow (kmol/s): %g\n", uds_flow_tot[1]);
printf("Total particle CO2 flow (kmol/s): %g\n", uds_flow_tot[2]);
fclose(fout);