REACTION KINETICS AND REACTOR MODELLING FOR CRUDE GLYCEROL AUTOTHERMAL REFORMING TO HYDROGEN RICH GAS

A Thesis

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In Partial Fulfillment of the Requirements

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in

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University of Regina

By

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Regina, Saskatchewan

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Anita Ninson Odoom, candidate for the degree of Master of Applied Science in Process Systems Engineering, has presented a thesis titled, Reaction Kinetics and Reactor Modelling for Crude Glycerol Autothermal Reforming to Hydrogen Rich Gas, in an oral examination held on March 14, 2019. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

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Abstract

Biomass as a source of hydrogen production has gained great cognizance amongst researchers. The growing trend of energy is geared towards renewable energy sources for which crude glycerol serves as a viable source for hydrogen production. The most widely studied feedstock for hydrogen production is methane (CH4). In this work, crude glycerol which is a bi product in biodiesel production is considered because it produces higher number of moles of hydrogen than methane and also, adds up to the effective use of crude glycerol as a source of hydrogen.

The kinetics for this system was studied over S/C ratio of 2.6 and O2/C 0.125 using 5% Ni/CeZrCa. Both power law and mechanistic kinetic models were studied. The overall power law model for crude glycerol autothermal reforming process was investigated with a pre-exponential factor of $4.3 \times 10^{10}$ mol/gcat.min and activation energy of $8.78 \times 10^4$ J/mol. The reaction orders with respect to crude glycerol, water and oxygen are 1.04, 0.54 and 1.78 respectively. The absolute average deviation of 5.84 % which showed a good correlation between the predicted and experimental rate. Afterwards, both power and mechanistic models were developed for steam reforming, total oxidation and CO2 Methanation. For steam reforming, Eley Rideal approach best described the rate with for the surface reaction step being the rate determining step (AAD<10 %). The kinetics of Total oxidation reaction was best described by the power law model with an AAD of less than 1 %. The mechanistic model that describes the TOR process was the molecular adsorption of crude glycerol with an AAD of 14.6 % via Langmuir Hinshelwood Hougou-Watson approach. CO2 methanation yielded an AAD of 5.8 % for the adsorption of carbon
dioxide (CO$_2$) by the Eley Rideal mechanism. There was no kinetic data on CO thus, the water gas shift reaction was not considered in this study.

Numerical modelling was performed based on the derived kinetics using both finite difference and finite element techniques. Both one (1) and two (2) dimensional reactor models were developed based on pseudo homogenous and heterogeneous models. The average absolute deviations obtained for one (1) dimensional model were 10% and 12.73% for pseudo homogenous and heterogeneous model respectively. For the 2–dimensional models, an AAD of 12.08 % for pseudo homogeneous and 13.1 % for heterogeneous was obtained where a 1-dimensional pseudo homogenous model was found to accurately model the fixed bed reactor. The results obtained were validated and it showed good correlation with experimental values. Thus, the obtained kinetic and numerical models accurately depict the system under study.
Acknowledgements

My foremost gratitude goes to my supervisor Dr. Hussameldin Ibrahim for his support and guidance during the period of my research. He steered me in the right direction with constructive criticism which always kept me on my toes in order to find solutions to meet the tight deadlines. Secondly, I would like to thank my co-supervisor, Dr. Amgad Salama for the great insight he provided me on the numerical section of this work. His office was always opened to me whenever I needed help and his words of encouragement during despairing times was just enough to get me back on track. I am also grateful to all my colleagues in Advanced Green Energy Research Group especially Emeka Nnabuo and Ishag Alawad for their suggestions and attentiveness to my Research problems and development. I would also to thank Prince Addo at StellenBorsch University, South Africa, Dr Abayomi Akande, James Coker, Daniel Afari and Michael Fabrik for brainstorming ideas with me. I would also like to thank my friends Jessica Narku Tetteh, Dr. Chikezie Nwaoha, Yomi Joel and Benjamin DeCardi Nelson for their encouragement.

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### List of Abbreviations and Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_g$</td>
<td>Gas Density, kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>Catalyst bulk density, kg/m$^3$</td>
</tr>
<tr>
<td>$u_z$</td>
<td>Velocity, m/s</td>
</tr>
<tr>
<td>$a_v$</td>
<td>Catalyst surface area per unit volume, 1/m</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Mass transfer coefficient of component j, m/s</td>
</tr>
<tr>
<td>$\partial t$</td>
<td>Time derivative, s</td>
</tr>
<tr>
<td>$\partial z$</td>
<td>Space derivative, m</td>
</tr>
<tr>
<td>$y_j$</td>
<td>Mole fraction of species, j</td>
</tr>
<tr>
<td>$C_{p_g}$</td>
<td>Specific heat capacity of the gas, J/kgK</td>
</tr>
<tr>
<td>$C_{p_p}$</td>
<td>Specific heat capacity of the catalyst, J/kgK</td>
</tr>
<tr>
<td>$h_f$</td>
<td>Heat transfer coefficient, W/m$^2$s</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Effective thermal conductivity of gas, W/mK</td>
</tr>
<tr>
<td>$D_{Lj}$</td>
<td>Axial mass dispersion, m$^2$/s</td>
</tr>
<tr>
<td>$D_{mj}$</td>
<td>Diffusion coefficient, m$^2$/s</td>
</tr>
<tr>
<td>$D$</td>
<td>Reactor diameter</td>
</tr>
<tr>
<td>$c_j$</td>
<td>Concentration of species j in bulk gas, mol/m$^3$</td>
</tr>
<tr>
<td>$c_{j,s}$</td>
<td>Concentration of species j on catalyst surface, mol/m$^3$</td>
</tr>
<tr>
<td>$L$</td>
<td>Reactor length</td>
</tr>
<tr>
<td>$w_j$</td>
<td>Mass fraction of species j in bulk gas, mol/m$^3$</td>
</tr>
<tr>
<td>$w_{j,s}$</td>
<td>Mass fraction of species j on catalyst surface, mol/m$^3$</td>
</tr>
</tbody>
</table>
$K_D$  Viscous pressure drop, Pa.s/m$^2$

$K_v$  Kinetic pressure drop, Pa.s$^2$/m$^3$

$K_p$  Inverse of viscous and kinetic pressure drop, Pa.s/m$^2$

$P$  Pressure, Pa

$T$  Temperature, K

SSEP  Self Sustained Electrochemical Promotion.

PH  Pseudo homogeneous

HET  Heterogeneous

ATR  Autothermal Reforming

SR  Steam Reforming

S/C  Steam to Carbon ratio

O$_2$/C  Oxygen to Carbon ratio

PLM  Power Law Model

ER  Eley-Rideal

LHHW  Langmuir-Hinshelwood-Hougen-Watson

TOR  Total Oxidation

RDS  Rate Determining Step

TR-BDF  Trapezoidal rule Backwards Differentiation Formulation

d$_p$  diameter of pellet
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_v$</td>
<td>Particle surface area to volume ratio, m$^2$/m$^3$</td>
</tr>
<tr>
<td>$\varepsilon_p$</td>
<td>Bedporosity</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Effectiveness factor</td>
</tr>
<tr>
<td>$\lambda_z$</td>
<td>Axial conductivity, J/s-m-K</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Viscosity</td>
</tr>
<tr>
<td>$\nu_j$</td>
<td>Stoichiometry of species, $j$</td>
</tr>
<tr>
<td>$N_{Re}$</td>
<td>Reynold number</td>
</tr>
<tr>
<td>$N_{Pr}$</td>
<td>Prandtl number</td>
</tr>
<tr>
<td>$N_{Sc}$</td>
<td>Schmidt’s number</td>
</tr>
<tr>
<td>$Sh$</td>
<td>Sherwood number</td>
</tr>
</tbody>
</table>
Chapter 1: Introduction

Hydrogen is the most plenteous and featherweight element on earth which is commonly attached to oxygen to form water and carbon to form hydrocarbons. It is colorless, odorless, nontoxic, tasteless, highly combustible and flammable. It exists as a diatomic gas which serves as a source of energy. Hydrogen has vast uses such as in fuel cell applications, petroleum refinery, metal treatment, fertilizer production, rocket fuel application, methanol and ammonia synthesis and processing of food (EIA, 2018)).

There are several techniques for hydrogen production namely reforming, water electrolysis and photocatalysis, pyrolysis, natural gas reforming, gasification and fermentation (Halabi et al., 2011). Hydrogen gas has great energy content per unit mass when compared to other fuels according to Sema (2018) and for this reason; hydrogen is termed as an energy carrier which has a promising future of serving as a substitute for transportation and power generation. H₂ has already gained a lot of research interest in its use for fuel cell application. The main problem with hydrogen production is its high production cost. The conventional transport fuels should be more expensive than hydrogen gas in order to dissuade people from purchasing them thus; the cost of production processes for Hydrogen should be reduced in order to make it viable.

Hydrogen can be produced from vast sources like fossil fuels, (natural gas and coal), nuclear energy and other renewable energy sources like biomass, wind, solar, geothermal, and hydro-electric (Energy.gov, 2019).
1.1 Background

Glycerol as a by-product of biodiesel production has enormous uses. Some of which includes; in food industries (as sweetener and food preservation), pharmaceutical application (cough syrup), personal care products, Liquid in electronic cigarette and so on. According to Advancedbiofuels.ca, 2019, “Biodiesel made in Canada reduces emissions significantly below those of fossil diesel, depending upon feedstock and production process.” From this, renewable energy sources help reduces carbon emissions produced from non-renewable sources. Benefits obtained from biodiesel are; renewability, biodegradability, reusability of waste products, reduction in greenhouse gases (80 % reduction based on life cycle), as well as little to no toxicity (Nrcan.gc.ca, c2015). Trif et al., (2016) stated the total amount of biodiesel produced in 2010 being more than 8 million metric tons but effective uses for the byproduct of biodiesel production is not readily available on the market according to Trif et al., (2016). In view of this, there is the need to find high value end products for crude glycerol production which will intend assure the sustainability of biodiesel.

Glycerol can be produced from hydrolysis of soap and fatty acids as well as transesterification of biodiesel. This research focuses on crude glycerol (glycerol with impurities) obtained from transesterification of biodiesel.

The growing trend of the biodiesel industry as observed from the year 1999 to 2009 is shown in figure 1-1.

The trend in figure 1-1 shows the amount of biodiesel produced in 1999 which was 9 % as against that produced in 2009 being 64 %. Finding effective uses for crude glycerol to
cater for the growing demands of the biodiesel will enhance its usage. Crude glycerol produced via biodiesel has some disadvantages which cannot be overlooked. A downside of crude glycerol produced from biodiesel is the presence of impurities such as methanol, salts, and free fatty acids among others. The presence of methanol in the crude glycerol makes the product hazardous and that goes further to increasing the purification cost and thus, purifying this kind of glycerol is very expensive. An analysis made by Ciriminna et al., 2014 estimated the cost of 98 wt % pure glycerol as $0.15/kg whilst the cost of a crude glycerol is $0.05/lb ($0.11/kg) according to West P.T, 2012. As such, finding effective uses for crude glycerol will harness the usage of biodiesel production which will in turn promote hydrogen production.
Figure 1-1: Trend in Biodiesel Industry from 1999-2009 (Ciriminna et al., 2014).
1.2 Motivation

The switch from non-renewable to renewable energy sources has attracted lots of research interests due to the adverse effects of non-renewable energy sources particularly fossil fuels on global warming and climate change. Biodiesel, a renewable energy source, with crude glycerol as its by-product is used in this work with the sole aim of contributing to hydrogen production.

Ghani et al., (2017) used crude glycerol (40 % pure glycerol) to produce $\text{H}_2$ via autothermal (ATR) process. Based on this work, the kinetics was studied for both power law and mechanistic models. This was dependent on the individual reactions which constitutes the ATR process. The development of the mechanistic kinetics explained the process involved in the catalysis. Also, from the experimental work, enough insight was not gained on the actual occurrences inside the reactor thus, numerical modelling was employed to offer great flexibility and analyze the reactor to obtaining in-depth knowledge of the process. This acquired knowledge will be useful for optimizing the process and enhance large scale production. This method is cheaper and faster than performing more experiments regarding optimizing the existing process. In this work, both MATLAB and COMSOL Multiphysics were used to comprehensively study and predict which model best mimicked the experimental work.

1.3 Objectives

The main objective of this thesis is to fully investigate the kinetics of autothermal reforming of crude glycerol. This will include deducing mechanistic models and providing thermodynamic scrutiny on the successful models.
Along with the kinetic model, a comprehensive numerical model for a fixed bed autothermal reforming reactor is conducted. At first, a two-dimensional model is considered using Comsol-multiphysics to highlight whether significant variations along the radius of the reactor occurred. Then, a one-dimensional model using Matlab is built to provide flexibility in data manipulation and to conduct parametric study.

1.4 Contributions

The contributions made in this work are;

- Develop a comprehensive reaction mechanism for autothermal reforming of crude glycerol.
- Develop a comprehensive numerical model for a fixed bed autothermal reforming reactor.

1.5 Thesis layout

Chapter 2 presents a general overview of the existing reforming techniques particularly steam reforming, partial oxidation, autothermal reforming and CO$_2$ Methanation. It also captures on fixed bed reactor modelling in general.

Chapter 3 describes the development of kinetic models from the criteria of plug flow conditions through to heat and mass transfer limitations. The independent reactions, power law and mechanistic models are all considered in this chapter. It gives more information on parameter estimation for the deduced kinetic models.
Chapter 4 deals mainly with reactor modelling. It includes both 1 and 2-dimensional fixed reactor modelling, the assumptions, governing equations in both MATLAB 2017 and COMSOL Multiphysics 5.2 a. The supporting equations for the reactor modelling are found in here.

Chapter 5 presents the results and discussions for the reaction kinetics which discusses the thermodynamic scrutiny of the realistic models and a comparison of their activation energies with literature. In addition, the results and discussions for the reactor modelling including validations, comparisons and temperature effects are included.

Chapter 6 outlines the limitations as well as conclusions and recommendations for further studies.
Chapter 2: Literature Review

2.1 Synopsis

This section captures the usefulness of hydrogen, technologies for hydrogen production and the benefits of using crude glycerol as a source for hydrogen production. Renewable energy sources are sources of energy that can be regenerated over a long period of time. US Energy Information Administration (EIA, 2017) categorized renewable energy into:

a. Biomass
   - Wood and wood waste
   - Municipal Solid Waste
   - Landfill gas and biogas
   - Ethanol
   - Biodiesel

b. Hydropower

c. Geothermal

d. Wind

According to EIA 2017, biodiesel is a biodegradable and nontoxic renewable energy source. When compared with fossil fuels, biodiesel produces less air pollutant (CO, SO₂, HCs etc.). Biodiesel is a carbon neutral fuel because it is basically obtained from plants which absorb CO₂ during their life cycle. Sources of biodiesel are enormous some of which are rapeseed, soybean, mustard, flax, sunflower, canola, palm oil, hemp, jatropha and
waste vegetable oils. According to the Environmental Protection Agency (EPA), biodiesel is the only commercial scale fuel categorized as an advanced biofuel due to its ability to reduce greenhouse gas emissions significantly in comparison to petroleum diesel thus, making it one of the most practical and cost-effective ways to immediately address climate change issues. (Biodiesel.org, 2019).

According to EIA, the energy consumption in the U.S as shown in figure 1 shows the energy consumed from 1776-2016. From the figures 2-1 and 2-2, it could be seen that wood, a typical biomass, was the primary source of energy for the U.S. During this period, there was reduced effect of greenhouse emissions until 1856 where petroleum, coal and natural gas were introduced in large quantities and hence, significant introduction to greenhouse gases and great influence on climate change.

Fossil fuels have a high consumption rate of energy in the US as compared to renewable energy (11%) as shown in figure 2-2. In the 11% of renewable energy composition, 45% is from biomass. Thus, increasing the usage in biomass as a renewable energy source can help curb greenhouse emissions and climate change menace to its minimum hence a motivation for this research.
Figure 2-1: U.S Energy consumption from 1776-2016

Figure 2-2: The various constituents of energy consumed by the U.S in 2016.
Adapted from: U.S Energy Information Administration, Preliminary data for April 2018 Monthly Energy Review.
Hydrogen can be produced via various technologies. Holladay et al., 2009 categorized the technologies as reforming hydrogen technologies (steam reforming, autothermal reforming, partial oxidation) and non-reforming hydrogen technologies (electrolysis of water, gasification, and pyrolysis) whereas Efstathiou and Kalamaras (2013) classified the technologies into H₂ from fossil fuels and H₂ from renewable resources (Biomass gasification, pyrolysis, electrolysis and thermosplitting of water). More information on these processes can be found in Holladay et al., (2009); Efstathiou and Kalamaras (2013); Bicakova and Straka (2012); Sema, (2018).

2.2 Reforming Technologies

2.2.1 Steam Reforming

Steam reforming is the most common reforming technique used for hydrogen production. Especially, steam methane reforming has obtained vast studies in literature over the past years. Steam reforming is a technique whereby the feedstock (hydrocarbon or oxygenated hydrocarbon) reacts with water in a reactor to produce valuable products. This process is a highly endothermic process signifying the huge energy requirements. A paramount factor in the steam reforming process is the Hydrogen (H): Carbon (C) ratio in the feedstock. A higher ratio implies a lower carbon dioxide emission (Efstathiou and Kalamaras, 2013).
Figure 2-3: Sources of Global Hydrogen Demand

Table 2-1: Summary of H₂ Production Techniques

<table>
<thead>
<tr>
<th>Process</th>
<th>Maturity</th>
<th>Efficiency</th>
<th>Raw material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Reforming</td>
<td>Commercialized</td>
<td>70-85 %</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Partial Oxidation</td>
<td>Commercialized</td>
<td>60-75 %</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Autothermal Reforming</td>
<td>Near term</td>
<td>60-75 %</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Plasma Reforming</td>
<td>Long term</td>
<td>9-85 %</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>Biomass Gasification</td>
<td>Commercialized</td>
<td>35-50 %</td>
<td>Biomass</td>
</tr>
<tr>
<td>Aqueous Phase Ref.</td>
<td>Mid term</td>
<td>35-55 %</td>
<td>Carbohydrate</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>Commercialized</td>
<td>50-70 %</td>
<td>Water + Electricity</td>
</tr>
<tr>
<td>Photolysis</td>
<td>Long term</td>
<td>0.5 %</td>
<td>Water + Sunlight</td>
</tr>
<tr>
<td>Thermochemical Water</td>
<td>Long term</td>
<td>NA</td>
<td>Water + Heat</td>
</tr>
</tbody>
</table>

(Efstathiou and Kalamaras, 2013)
2.2.1.1 Literature on Steam Reforming

Sa et al. (2011) studied the kinetics of methanol via steam reforming and reversed Water Gas Shift (rWGS) with CuO/ZnO/Al₂O₃. The rate law expressions regressed in their paper was based on already existing literature. The kinetic parameters were found by nonlinear regression. The heat of adsorption values and the other constants were obtained by regression. The removal of hydrogen from methoxy which is represented by the adsorption of methanol on the active site was found to be the rate determining step.

Sundari and Vaidya (2012) studied the kinetics of glycerol via steam reforming with Ru/Al₂O₃ catalyst. In their work, the primary reaction were the decomposition of pure glycerol and water gas shift:

\[ C_3H_8O_3 \leftrightarrow 4H_2 + 3CO \quad \Delta H_{25^\circ C} = 251 \frac{kJ}{mol} \]  
\[ CO \leftrightarrow H_2 + CO_2 \quad \Delta H_{25^\circ C} = -41 \frac{kJ}{mol} \]  
\[ 4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H_{25^\circ C} = -165 \frac{kJ}{mol} \]

In deriving mechanistic equation, the process description was categorized into:

- Glycerol adsorption on catalyst surface
- Removal of hydrogen (dehydrogenation) from catalyst surface
- Scission of C-C or C-O bond which might produce alcohols or alkanes
- Removal of hydrogen (dehydrogenation) from process to produce carbon monoxide or dioxide
- Surface reaction of carbon monoxide or dioxide with water which will further undergo water gas shift, methanation or simply desorption process.
The conditions for their studies were temperature of 350-500 °C and steam to glycerol ratio of 3-12. Single site Eley-Rideal (ER) model and steady state hypothesis were used to obtain the rate law expression pure glycerol.

In 2010, Cheng et al. developed an intensive study for the kinetics of steam reforming of glycerol using Co-Ni/Al₂O₃ catalyst. The parameters over which this study was done are s/c (3-12), temperature (773 and 823) and 1 atm pressure. Power law, single and dual site Eley-Rideal (ER) and Langmuir-Hinshelwood (LHHW) models were derived. The rate law expression was written in terms of the adsorption steps. The possible reactions are described below:

Overall Steam reforming

\[ C_3H_8O_3 + 3 H_2O \leftrightarrow 7 H_2 + 3 CO_2 \] (2.4)

Decomposition of glycerol

\[ C_3H_8O_3 \leftrightarrow 4 H_2 + 3 CO \] (2.5)

Water Gas Shift Reaction

\[ CO + H_2O \leftrightarrow H_2 + CO_2 \] (2.6)

Hydrogenation of Crude Glycerol

\[ 2 C_3H_8O_3 + H_2 \leftrightarrow 3 CH_4 + 3 H_2O + 3 CO \] (2.7 a)

\[ 2 C_3H_8O_3 + H_2 \leftrightarrow 3 CH_4 + 3 H_2O + 3 CO \] (2.7 b)

Other Reactions

\[ CO + 3H_2 \leftrightarrow CH_4 + H_2O \] (2.8 a)
\[ CO_2 + CH_4 \leftrightarrow 2 CO + 2H_2 \]  
\[ C + H_2O \leftrightarrow H_2 + CO \]  
\[ \text{CO}_2 \text{ Methanation} \]
\[ CO_2 + 4H_2 \leftrightarrow 3CH_4 + 2H_2O \]
\[ \text{Decomposition Reactions} \]
\[ 2CO \leftrightarrow C + CO_2 \]
\[ CH_4 \leftrightarrow 2H_2 + C \]

The derived mechanisms composed of a series of reaction steps were based on both molecular adsorption and dissociative adsorption. The rate law expression was derived and regressed to estimate the parameters which showed good agreement with literature.

Bakhtiari et al. (2015) studied kinetics of oxygenated hydrocarbon via steam reforming using Ni/CeZrGdO\textsubscript{2} catalyst in a packed bed reactor. The conditions for this study were steam to feed ratio of 2-6, temperature range of 550-600 °C at atmospheric pressure. Power law and Eley Rideal models were studied for this process. The rate controlling step was determined as the dissociative adsorption of oxygenated hydrocarbon. The reaction mechanism was summarized as adsorption (molecular and dissociative) and surface reaction step.
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Catalyst</th>
<th>Observation and Comment</th>
<th>Reference</th>
</tr>
</thead>
</table>
| N/A           | Ni based          | • Glycerol SR and Sorption Enhanced Glycerol SR.  
• Dual site LHHW model and Power Law were deduced.  
• Reviewed other literature and suggested more research should be done in this area.                                        | Silva et al., (2015) |
| 823-923 K     | Ni-based          | • Steam Reforming of Ethanol.  
• Only power law model was determined in this work and LHHW for future works.                                                                                                                                       | Veronica et al., (2008) |
| 473-873 K     | Ni-based          | • Ethanol steam reforming.  
• Dissociative adsorption of methane as the rate development step.  
• Developed new LHHW to clarify, make easy and outperform the complexity in other models  
• LHHW produced better results than PLM.                                                                                                                        | Wu et al., (2014)   |
| 873-923K      | Ni-based (Ni-Al-O) | • Both reversible and irreversible rate law expressions were derived.  
• Bio-ethanol steam reforming was studied.  
• LHHW approach was studied and the surface reaction step was the rate determining step.                                                                  | Llera et al., (2012) |
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Catalyst</th>
<th>Observation and Comment</th>
<th>Reference</th>
</tr>
</thead>
</table>
| 873-1073K   | Ru/Al₂O₃                 | • Glycerol reforming via supercritical water reforming was studied.  
• Steady state hypothesis was used to derive the rate law expression.                                                                                      | Byrd et al., (2008)         |
| 573-973K    | Ni/Al₂O₃                 | • Methane steam reforming was based on Xu and Froment.  
• LHHW model was used to derive rate law expression and further used for numerical modelling.                                                              | Abbas et al., (2017)        |
| 873-973 K   | Using Ni based Ce-Zr support catalyst. | • Ethanol steam reforming was studied.  
• ER and PLM models were tested.  
• The ER mechanism included; dissociative adsorption, dissociative adsorption of adsorbed intermediate on vacant site and surface reaction steps.  
• The RDS was the adsorption of ethanol on active site.                                                                 | Patel et al., (2013)        |
| 723-823K    | Rh/CeO₂/Al₂O₃            | • Studied Ethanol steam reforming in microchannel reactor.  
• RDS was the surface reaction step described between adsorbed ethanol intermediate and adsorbed water.  
• Mainly ethanol and methane adsorption were considered for their paper.                                                                                   | Peela and Kunzru, (2011)    |
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Catalyst</th>
<th>Observation and Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>• The overall equation for each step was assumed to be an elementary reaction thus; the stoichiometric coefficient of the species was the reaction order.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• LHHW mechanism best described the process.</td>
<td></td>
</tr>
<tr>
<td>673-863 K</td>
<td>Ni-based catalyst</td>
<td>• Studied the kinetics of crude ethanol. Tested both ER and LHHW models.</td>
<td>Akpan et al., (2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• 4 out of 11 models were successful and further used for mathematical modelling which gave good agreement with experimental data.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• The kinetics was best described by Eley Rideal</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• RDS was the dissociative adsorption of crude ethanol on active site of Ni catalyst</td>
<td></td>
</tr>
<tr>
<td>823-923 K</td>
<td>Ni based</td>
<td>• Studied Ethanol steam reforming where two (2) different sets of LHHW models were studied and the surface reaction step was found to be the RDS.</td>
<td>Mas et al., (2008)</td>
</tr>
</tbody>
</table>
2.2.2 Oxidative Reforming

Oxidative reforming is a reforming process whereby the hydrocarbon reacts in the presence of limited or total supply of oxygen to form \( \text{H}_2 \) and carbon monoxide (CO) or \( \text{CO}_2 \) for the latter one (Holladay et al., (2009)). This process is highly exothermic and has high tendencies for coke formation and sintering thus, the selection of catalyst for this process is vital. There exists some work in literature in which different feedstock are used for this process. Some of which were methane, diesel and isoctane. The most common catalysts used for partial oxidation process are Nickel and Rhodium. (Bicakova and Straka, 2012).

2.3.2.1 Literature on Oxidation Reforming

There exists a lot of literature on oxidation of natural gas and liquid fuel. Below are a few examples on oxidative reforming process:

Hu and Ruckenstein (1996) investigated the kinetics of methane using partial oxidation in a differential reactor under unsteady state condition. The temperature range for the study was 723-923 K under atmospheric pressure. They reported a typical heat of reaction as -22.6 kJ/mol which conforms to a typical exothermic reaction. Their reaction was summarized as:

- The dissociative adsorption of Oxygen on an active site.
- Dissociative adsorption of methane on an active site to form an adsorbed intermediate and the further dissociation into C and H atoms.
- Surface reaction of C and O atom to form targeted products (CO formation found to be RDS).
• Desorption of adsorbed products from active site.

It was concluded from the response curves that the generation of CO is the RDS because the rate of production of CO is slower than the rate of consumption. The rate of production of CO is the slowest step and thus, the RDS.

Dinh et al (2017) studied the kinetics of diesel fuel via partial oxidation supported by plasma. They came up with a diesel chemical formula as $C_{12}H_{23}$ where the overall stoichiometric equation was given as the below considering the effect of $O_2/C$ ratio.

$$C_{12}H_{23} + 6 (O_2+3.76 N_2) \rightarrow \text{Products}$$

A power law model was first used to find the pre-exponential factor and activation energy. There was no information about mechanistic models in their work. The effects of $O_2/C$ on selectivity and fuel conversion were studied. It was concluded that, there was a high probability that $O_2/C$ ratio determined the heat of reaction, but the electrical energy transformed into thermal energy is much more influential than heat of reaction via oxidation reaction.

Ibrahim and Idem (2006) researched on hydrogen production using Ni/Al$_2$O$_3$ catalyst with isooctane as feedstock via partial oxidation route. Their study was at atmospheric pressure, 863-913 K temperature range, and W/FAO range of 7.09-30.86 kg /mol and $O_2/C_8H_{18}$ ratio of 4. They modelled both LHHW and ER methods where single site LHHW model with a surface reaction of adsorption of isooctane and oxygen (dissociation adsorption for the former and molecular adsorption for the latter) was the RDS. The overall stoichiometric equation was given as;

$$C_8H_{18} + 4 (O_2+3.76 N_2) \leftrightarrow 8 \text{CO} + 9 \text{H}_2 +15.04 \text{N}_2$$ (2.11)
Power law model based on an irreversible reaction was given by Arrhenius law as:

\[ r = k_0 f e^{-\left(\frac{E_f}{RT}\right)} P_{C_8H_{18}}^m \]  

(2.12)

Among the 18-different rate law expression derived, model 14 well suited the experimental data with an average absolute deviation of 6.4%. The rate law expression derived for the RDS:

\[ r = \frac{k_0 f e^{-\left(\frac{E_f}{RT}\right)} C_{C_8H_{18}}^{1.5}}{\left[1 + (K_{C_8H_{18}} C_{C_8H_{18}})^{0.5}\right]} \]

(2.13)

These same authors analyzed the kinetics of gasoline (C_{8.27}H_{15.1}) over Ni-CeO_2 catalyst using partial oxidation. The O_2/C ratio was varied between 0.25-1, 1 atm pressure, 673-1023 K as the operating conditions in a fixed bed reactor. In this work, they checked the applicability of their former models on this gasoline mixture and it limited the models to only 12 (10 LHHW and 2 ER models). In developing the power law model, they used the most abundant component in the surrogate fuel (C_{8H_{18}}) and the power law rate law expression was given as:

\[ r = k_0 f e^{-\left(\frac{E_f}{RT}\right)} P_{C_8H_{18}}^m P_{O_2}^n P_{CO}^o P_{H_2}^p f^q \]

(2.14)

Model 10 which was a LHHW model for a surface reaction step between dissociated adsorption product of surrogate gasoline and Oxygen. It was a dual site mechanism given in table 2-4.

In their work, only H_2 and CO are considered in the mechanism whereas, the probability of methane being formed could also be considered. Mechanism 10 was chosen because its
activation energy was close to that of the power law model and, this model fitted well with the experimental data.

Oluku et al., (2018) studied the kinetics of diesel via partial oxidation using a metallic oxide catalyst. In their work, the obtained rate law expression was further used to model the reactor. The Eley-Rideal model with an RDS of dissociative adsorption of diesel on the active site and a power law model were tested. The overall reaction for the partial oxidation was given by equation 2.15. Also, they tested for both LHHW and ER model which yielded a total of 10 mechanisms. They are summarized as well in table 2-5.

\[
C_{16}H_{34} + 8 O_2 \leftrightarrow 16CO + 17 H_2 \quad \Delta H = -1319 \frac{kJ}{mol} \tag{2.15}
\]

All the mechanisms have adsorption, surface reaction and desorption steps. The differences between the LHHW models are molecular adsorption of LHHW 1 and dissociative adsorption of LHHW 2 for the main feedstock and the opposite for the adsorption of Oxygen. The successful model after the thermodynamic scrutiny using Boudart-Mears-Vannice (BMV) guidelines was the ER model with adsorption of diesel on the active site. The AAD reported was below 9% for both models.
Table 2-3: Mechanism and rate law expression of partial oxidation of diesel surrogate

| Mechanism 10 | \[ \begin{align*} 
C_aH_b + S & \leftrightarrow C_aH_b.S \\
C_aH_b.S + S & \leftrightarrow C_{a-1}H_{b-n_2}.S \\
+ C_{n1}H_{n_2}.S & \end{align*} \] | \[ \begin{align*} 
r & = \frac{k_{0f} e^{-\frac{E_f}{RT}}}{C_A} \left[ C_A^4 C_B^4 - C_D C_C \frac{K_{eq}}{K_C} \right] I^q \\
& \quad \left( \left( 1 + K_A C_A + K_B C_B + K_C C_C + \left( \frac{K_B C_B}{C_D} \right)^2 \right)^2 \right) \end{align*} \] |

| | \[ \begin{align*} 
O_2 + 2S & \leftrightarrow O.S + O.S \\
+ C_{n1}H_{n_2}.S & \\
O.S & \leftrightarrow C_{n1}H_{n_2-1}O.S + H.S \\
+ C_{n1-1}H_{n_2-1}.S & \\
C_{n1}H_{n_2-1}O.S + S & \leftrightarrow C.O.S \\
+ C_{n1-1}H_{n_2-1}.S & \\
C_{n1-1}H_{n_2-1}.S + O.S & \leftrightarrow C_{n1-1}H_{n_2-2}.S + H.S \\
H.S + H.S & \leftrightarrow H_2 + 2S \\
CO + S & \leftrightarrow CO + S \end{align*} \] |

Table 2-4: Mechanism of partial oxidation of diesel in literature.

<table>
<thead>
<tr>
<th>ER model</th>
<th>LHHW 1</th>
<th>LHHW 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{16}H_{34} + 16* \leftrightarrow 14CH_2* + 2CH_3*</td>
<td>C_{16}H_{34} + * \leftrightarrow C_{16}H_{34}*</td>
<td>C_{16}H_{34} + 16* \leftrightarrow 14CH_2* + 2CH_3*</td>
</tr>
<tr>
<td>14CH_2* + 7O_2 \leftrightarrow 14CO + 14 \ H_2*</td>
<td>8O_2 + 16* \leftrightarrow 8O* + 8O*</td>
<td>8O_2 + 8* \leftrightarrow 8O_2*</td>
</tr>
<tr>
<td>2CH_3* + O_2 \leftrightarrow 2CO + 3H_2 + 2*</td>
<td>C_{16}H_{34}* + 8O* \leftrightarrow 17H_2 + 8C_2 O* + *</td>
<td>2CH_3* + O_2* \leftrightarrow 2CO + 3H_2 + 3*</td>
</tr>
<tr>
<td></td>
<td>16CO* \leftrightarrow 16CO + 16*</td>
<td>14CO* \leftrightarrow 14CO + 14*</td>
</tr>
</tbody>
</table>
Table 2-5: Some existing literature on Partial oxidation

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rate Law Expression</th>
<th>Observation and Comment</th>
<th>Reference</th>
</tr>
</thead>
</table>
| 1123-1223K    | \( r = k_0 f e^{-\frac{E_f}{RT}} \left( \frac{C_A}{C_A^\text{eq}} \right)^2 \left( \frac{1+K_A C_D + K_B \left( \frac{C_c C_D}{C_B^{1.5}} \right)}{1+K_A C_D + K_B \left( \frac{C_c C_D}{C_B^{1.5}} \right)+K_C \left( \frac{C_c C_B^{1.5}}{C_B^{1.5}} \right)} \right)^{16} \) | • Adsorption of diesel on active site as the RDS.  
  • PLM and the ER model produced accurate results which gave good comparison with experimental data. | Oluku et al., (2018) |
| 923 K         | \( r = \rho_0^2 \times 1.9 \times 10^{10} \times PCH_4 \left( 1 + \left( 1.9 \times 10^{10} \times \frac{PCH_4}{9 \times 10^7 \times PO_2} \right)^2 \right) \) | • Dual site LHHW model.  
  • Dissociative adsorption of CH_4 on active site as the RDS. | Arena et al., (2000) |
| 973 K         | N/A                                                                                | • ER kinetic model studied over Li/MgO catalyst.  
  • Model predicted conversion, product distribution, and produced good validation with experimental work. | Tjatjopoulos and Vasalos, (1992) |
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Rate Law Expression</th>
<th>Observation and Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>548-723 K</td>
<td>N/A</td>
<td>• Pseudo 1(^{st}) order rate was used in the prediction of kinetic parameters</td>
<td>Messerer et al., (2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• No information on rate law expression.</td>
<td></td>
</tr>
<tr>
<td>573-1123 K</td>
<td>[ r = \frac{k_{C_{3}H_{8}}P_{C_{3}H_{8}}}{1 + K_{H_{2}O}P_{H_{2}O}} \sigma_{O_{2}} ]</td>
<td>• Studied kinetics and reactor modelling of C(<em>{3})H(</em>{8}). The mechanism used for rate law expression was not mentioned</td>
<td>Pagani et al., (2012)</td>
</tr>
<tr>
<td>723-93 K</td>
<td>[ r = k \frac{K_{A}K_{B}P_{A}P_{B}}{(1 + K_{A}P_{A} + K_{B}P_{B})^{2}} ]</td>
<td>• Kinetics using LHHW was studied for the reaction involving SSEP catalyst.</td>
<td>Huang et al., (2012)</td>
</tr>
<tr>
<td></td>
<td>[ \text{where } A = C_{15}H_{32} ]</td>
<td>• These models predicted quantitatively the fuel conversion of the POX process. No information about the RDS is mentioned.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ B = O_{2} ]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2.2.3 Autothermal Reforming

Autothermal Reforming (ATR) is a combination of steam reforming and partial oxidation processes. The partial oxidation process occurs provides the heat absorbed by the steam reforming process thus making the whole process thermally self-sustaining. Increasing the Oxygen to feed ratio reduces the external heat requirement needed to enable thermoneutral conditions. A typical stoichiometric equation for autothermal is dependent on reaction conditions and is shown below:

$$C_3H_8O_3 + a O_2 + b H_2O \rightarrow c CO + d CO_2 + e H_2 + fCH_4$$  \hspace{1cm} (2.16)

$$a-f = f$$ (reformer temperature; steam to carbon ratio (S/C); oxygen to carbon ratio ($O_2/C$))

(Gutierrrez Ortiz et al., 2011).

2.2.3.1 Existing Literature on Glycerol Autothermal Reforming

Authayanun et al. (2010) performed thermodynamic studies on hydrogen production for fuel cells using crude glycerol via autothermal reforming. The constituent of crude glycerol was dependent on the raw material used for biodiesel production. The parameters analyzed were operating temperature, oxygen to feed (crude glycerol) ratio and steam to feed (crude glycerol) ratio. From their work, the crude glycerol was modelled as pure glycerol and methanol and different reaction schemes were written for the various reactions.

1. Steam reforming
   - $$C_3H_8O_3 + 3 H_2O \leftrightarrow 7 H_2 + 3 CO_2$$  \hspace{1cm} (2.17 a)
   - $$CH_3OH + H_2O \leftrightarrow 3 H_2 + CO_2$$  \hspace{1cm} (2.17 b)

2. Oxidation
   - $$C_3H_8O_3 + \frac{3}{2} O_2 \leftrightarrow 4 H_2 + 3 CO_2$$  \hspace{1cm} (2.18 a)
\[ CH_3OH + \frac{1}{2} O_2 \leftrightarrow 2 H_2 + CO_2 \]  

(2.18 b)

3. Water Gas Shift

\[ CO + H_2O \leftrightarrow H_2 + CO_2 \]  

(2.19)

4. Methanation

\[ CO + 3 H_2 \leftrightarrow H_2O + CH_4 \]  

(2.20)

5. Methane dry reforming

\[ CO_2 + CH_4 \leftrightarrow 2H_2 + 2CO \]  

(2.21)

However, the product composition in their studies was solely based on thermodynamic analysis leaving out the effects of the catalyst. They wound up their paper by stating an approximate range of \( O_2/C \) ratio as 0.4-0.7 which was subjected to the impurities found in the crude glycerol. Increasing the amount of steam, increases the amount of Oxygen required to support the autothermal reformer.

Liu and Lawal (2015) developed kinetics for ATR using glycerol in a monolith catalyst. Negligible mass and heat transfer limitations in kinetic region as well as the rate law expression was based on the Langmuir Hinshelwood mechanism. The operating conditions was at 650 °C temperature, steam to carbon ratio of 0.4, oxygen to carbon ratio of 0.15 and a pressure of 1 atm. Six different lengths and three (3) different variations in temperature made for each catalyst length, S/C and \( O_2/C \) were all varied. The atomic matrix approach was used to determine the number of independent reactions which could be used to describe the auto thermal reforming reactions. They arrived at these feasible reactions;

1. Steam Reforming

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

(2.22)
2. Oxidation

\[ C_3H_8O_3 + 2O_2 \leftrightarrow 4H_2 + 3CO \]  

(2.23)

3. Water Gas Shift

\[ CO + H_2O \leftrightarrow H_2 + CO_2 \]  

(2.24)

In their performance study, it was discovered that all the oxygen was depleted for a catalyst weight of 0.012g. Thus, for a catalyst weight above 0.012g, only steam reforming and water gas shift reactions were modelled. The development of the LHHW was based on both single and dual site considering the adsorption, surface reaction and desorption mechanisms. Also, the removal of water from glycerol molecule, the likelihood of OH adsorption on active site is probable. The main difference in models was in the type of adsorption (dissociative or non-dissociative) on the active site. Polymath was used to regress the kinetic data for the estimation of parameters. Afterwards, thermodynamic and optimization constraints \( K_{ads}k_j > 0; E_{activation} > 0; R^2 > 95 \% \text{ and standard errors} \ll \text{the estimates} \) were used to ensure the parameters estimated were reasonable.
<table>
<thead>
<tr>
<th>Temperature and Catalyst</th>
<th>Rate Law Expression</th>
<th>Observation and Comment</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Cu/ZnO/CeO$_2$/Al$_2$O$_3$ 473-573 K | Available in reference. | • Oxidative steam reforming of methanol.  
• LHHW approach was used to discover three (3) models obtained from 2 mechanisms. These were categorized as steam reforming, partial oxidation and reverse Water Gas Shift. | Patel and Pant, 2009. |
| 1023-1173 K | N/A | • Mechanistic study of tetradecane (C$_{14}$H$_{30}$) via autothermal reforming  
• Hydrogen production is remarkably influenced by partial oxygen and water gas shift reaction (minor effect). | Dorazio and Castaldi, 2008 |
| Rh-Ni/CeO$_2$-ZrO$_2$ catalyst | Available in reference | • Kinetics of bioethanol via oxidative steam reforming was studied using LHHW technique.  
• This model was sub categorized into oxidative steam reforming, Ethanol decomposition and water-gas shift reactions. | Mondal et al., (2016) |
<table>
<thead>
<tr>
<th>Temperature and Catalyst</th>
<th>Rate Law Expression</th>
<th>Observation and Comment</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Pd-Zn/ Al₂O₃             | $r_{tor} = \frac{k_1 y_{DME} y_{O_2}}{(1 + K_{H_2O} y_{H_2O})^2}$ | • Power Law Model and LHHW models were developed.  
• Lsqnonlin function in MATLAB 7.1 was used for parameter estimation.  
• Independent reactions were chosen as total oxidation, steam reforming, Methanol and DME decomposition, water-gas shift. | Creaser et al., 2010 |
<p>|                         | $r_{SR} = \frac{k_2 y_{DME} y_{H_2O}}{(1 + K_{H_2O} y_{H_2O})^2}$ |                           |           |
|                         | $r_{meth} = \frac{k_3 y_{CH_3OH}}{(1 + K_{H_2O} y_{H_2O})}$ |                           |           |
|                         | $r_{WGS} = \frac{k_4 y_{CO} y_{H_2O}}{(1 + K_{H_2O} y_{H_2O})^2} \left(1 - \frac{y_{CO} y_{H_2} y_{H_2O}}{y_{CO} y_{H_2} K_{eq}}\right)$ |                           |           |
|                         | $r_{DME} = \frac{k_5 y_{DME}}{(1 + K_{H_2O} y_{H_2O})}$ |                           |           |
| No information on catalyst used | Available in reference. | • Autothermal reforming of n-hexadecane was studied. | Shi et al., 2009 |</p>
<table>
<thead>
<tr>
<th>Temperature and Catalyst</th>
<th>Rate Law Expression</th>
<th>Observation and Comment</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Pt/ Al₂O₃ 1023-1173 K.    | Available in reference | • Kinetics of tetradecane via LHHW approach was studied.  
• The reactions involved are total oxidation, steam reforming and water gas shift reactions.  
• The rate law expression for total oxidation was represented by power law model (since it’s assumed to be a cumulative of partial oxidation, WGS and hydrogen oxidation) whereas the other 2 models were subjected to LHHW. | Parmar et al.,2010 |
<table>
<thead>
<tr>
<th>Temperature and Catalyst</th>
<th>Rate Law Expression</th>
<th>Observation and Comment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/Ni catalyst 773-1023 K</td>
<td>$r = \frac{kK_A P_A P_B}{1 + K_A P_A}$</td>
<td>• Power law and Eley-Rideal models yielded good results in correlation with experimental data.</td>
<td>Gawade et al., 2010</td>
</tr>
</tbody>
</table>
2.2.4 CO₂ Methanation (CO₂ Hydrogenation)

Auto-thermal reforming reaction is a universal reforming process consisting of sub reforming processes namely steam and oxidation reforming. The possibility of methane formation as a possible reaction in the process cannot be left out. The process by which we have methane forming in such a process is via CO/CO₂ hydrogenation. There is a vast literature existing on dry (CO₂) reforming of methane which is an endothermic reaction Pakhare et al., (2014); Sadykov et al., (2011); Ayodele et al., (2017); Abdullah et al., (2017) whereas CO₂ hydrogenation is an exothermic reaction (Saeidi et al. (2017); Weatherbee and Bartholomew, (1982); Jacquemin et al., (2010); Fujita et al., (1993)).
The reaction is given by;

\[
\text{CO}_2 + 4 \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H_{25^\circ C} = -165 \text{ kJ/mol (CO}_2\text{ Methanation)} \quad (2.25)
\]

\[
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4 \text{H}_2 \quad \Delta H_{25^\circ C} = -165 \text{ kJ/mol (dry reforming of methane)} \quad (2.26)
\]

2.3.4.1 Existing literature on CO₂ Methanation

The kinetics on CO₂ Methanation has been studied over a vast range of temperature and different catalysts. Pakhare at al., (2017) reported on the activity catalyst and withstanding potentials to carbon formation in increasing order as Fe, Cu< Ni, Pt, Pd< Ru, Rh. This list of catalyst provides an insight on the type of catalyst to choose for CO₂ methanation based on the desired activity. A table below summarizes the rate law expression, reaction mechanism as well as some inferences obtained from literature

Kathiraser et al., (2015) studied the kinetics of methane via CO₂ reforming using Ni catalyst. In their work, they did a review on some works in literature for CO₂. The kinetic models presented were based on Langmuir Hinshelwood Hougen Watson (LHHW), Eley
Rideal and the power law. From this work, they established that, knowing the properties of the catalyst is a requirement for effective operation of the system. The temperature range was 500-900 °C, a feed ratio of 1:1 and a pressure of 1 atm. This process represents an endothermic reaction where temperature greatly affects the system. Before developing a mechanistic model, a power law model was first obtained. It was concluded from the power law model that, methane was more adsorbed on the catalyst and had greater influence on the kinetics than the other species. Appropriate mechanisms were derived for the mechanistic model development. Nonetheless, the power law model on the plus side has an easy and simple application for parameter estimation whereas, the mechanistic technique is useful when a vast range of partial pressures exist and the knowledge of understanding the reactions occurring is necessary. The steps considered were

- Dissociation of reactants on catalyst
- Adsorption of intermediates on active sites
- Surface reaction between adsorbed intermediates and desorption of products.

Inferences made were that LHHW model best described the kinetics. Also, the availability of ‘quality’ experimental data can enhance the determination of mechanistic models.
Table 2-7: Summary of Literature on CO₂ Methanation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rate Law Expression</th>
<th>Focus</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Ni-based catalyst 473-503 K | \( r = \frac{k_0 e^{-\left(\frac{E_a}{RT}\right) P_{CO_2}}}{1 + K_{CO_2} P_{CO_2}} \) | - LHH model was used and the RDS was the adsorption of CO₂.  
- Desorption and surface reaction controlled the rate at high concentration. | Herwijnen et al., (1972) |
| Ni-Al₂O₃ 443-483 K 20 Bar | \( r = \frac{a P_{CO_2}^{0.5} P_{H_2}^{0.5}}{(1 + b_1 P_{H_2}^{0.5} + c_1 P_{CO_2}^{0.5} P_{H_2}^{0.5} + d_1 P_{H_2} O)^2} \) | - RDS is dissociative adsorption of CO          | Lim et al., (2016) |
| 573-673 K       | \( r = \frac{k_3 P_{CH_4} P_{H_2} O^2 - \frac{P_{H_2} P_{CO_2}}{K_{eq}}}{(1 + K_{1} P_{CO_2} + K_{2} P_{CH_4} + K_{3} P_{H_2} + K_{4} P_{H_2} O^2)^2} \) | - The RDS was the surface reaction step.          | Xu and Froment (1989) |
| N/A Ni/Al(O)ₓ   | \( r = \frac{k_0 P_{CO_2}^{0.5} P_{H_2}^{0.5}}{(1 + K_{1} P_{CO_2}^{0.5} + K_{2} P_{H_2}^{0.5} + K_{OH} P_{H_2} O)^2} \) | - LHHW mechanism and power law model were both tested.  
- The COH formation was the RDS.                | Koschany et al., (2016) |
<p>| 523-623 K       | ( r = \frac{k_0 P_{CO_2}^{0.5} P_{H_2}^{0.5}}{(1 + K_{OH} P_{H_2} O^2)^2} \left(1 - \frac{P_{CH_4} P_{H_2} O^2}{K_{eq} P_{H_2} P_{CO_2}}\right) ) | - LHHW mechanism was used for rate law development where OH was the most abundant species. | Miguel et al., (2018) |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rate Law Expression</th>
<th>Focus</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni based</td>
<td>$r = \frac{k_3(PH_2^2 - \frac{PCH_4^{0.5}PH_2O}{K_{eq}(PCO_2^{0.5})})}{(1 + K_1 \frac{PCH_4^{0.5}PH_2O}{PH_2^2})}$</td>
<td>• Analyzed different existing models based on Ni based catalyst.</td>
<td>Kathiraser et al., (2015)</td>
</tr>
<tr>
<td>443-473 K</td>
<td>$r = \frac{k_0PCOPH_2}{(1 + K_{CO}PCO + K_{H_2}PH_2)^2}$</td>
<td>• Rate law expression was based on existing LHHW models in literature. The models were regressed to find the best fit with experimental data.</td>
<td>Lim et al., (2016)</td>
</tr>
<tr>
<td>523-623K</td>
<td>$r = \frac{k_0PCO_2^{0.5}PH_2^{0.5}}{(1 + K_{OH}PH_2^{0.5})^2} \left(1 - \frac{PCH_4PH_2O^2}{K_{eq}PH_2^2PCO_2}\right)$</td>
<td>• LHHW models were tested and the rate law expression was based on the most abundant reactive species. • Hydroxyl was the MARI which yielded the best results that fitted experimental data.</td>
<td>Miguel et al., (2018)</td>
</tr>
</tbody>
</table>

*MARI== most abundant reactive intermediate*
Figure 2-4: Autothermal Reforming Process. Adapted from: Efstathiou, A.M and Kalamaras, M.C (2013)

Table 2-8: Differences Between the major reforming Techniques.

<table>
<thead>
<tr>
<th>Technology</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Steam Reforming</td>
<td>• Produces higher hydrogen yield</td>
<td>• Highly endothermic process.</td>
</tr>
<tr>
<td></td>
<td>• Most widely used and commercialized technology</td>
<td>• The high energy requirement and equipment purchase makes the process cost intensive.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Sintering of catalyst</td>
</tr>
<tr>
<td>2. Auto thermal Reforming</td>
<td>• Thermo neutral process.</td>
<td>• Slightly lower yield of hydrogen compared to Steam reforming</td>
</tr>
<tr>
<td></td>
<td>• Low or no coke formation based on adjustment of O/C and S/C.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Low energy requirement making the overall process have a lower capital cost.</td>
<td></td>
</tr>
<tr>
<td>3. Partial Oxidation</td>
<td>• No catalyst needed.</td>
<td>• Low hydrogen yield.</td>
</tr>
<tr>
<td></td>
<td>• Simple, commercialized and easy-to-practice technology.</td>
<td>• There is a high possibility of catalyst deactivation due to coke formation.</td>
</tr>
</tbody>
</table>

(Holladay et al., (2009); Efstathiou, A.M and Kalamaras, M.C (2013)
2.3 Reactor Modelling

2.3.1 Synopsis

Reactor modelling has attracted vast studies especially the catalytic packed bed tubular reactor (PBTR), which is often used for both hydrocarbon and oxygenated hydrocarbon reforming (Aboudheir et al., 2006; Bischoff and Froment, 1990). The packed bed reactor is an example of a catalytic reactor. This is a tube or vessel containing uniform catalyst pellets in a fixed position forming a catalyst bed for reactions (Rase, 1990; Lordanidis, 2002; Gianpiero et al., 2015; Hochgesand, 1989). Advantages of packed bed reactors, which make them attractive in industrial processes are; simplicity of design, higher conversion, little to no maintenance due to the absence of wear out of movable parts and low operation cost. However, number of disadvantages also exists including: channeling in the reactor, difficulty to clean and change catalyst, presence of undesirable end products and imperfect temperature control (Bartal et al., 2009).

For a reaction to take place, the bulk fluid is discharged into the reactor where it passes through the void spaces of the bed. The reactants present in the bulk fluid are conveyed unto the catalyst where they adsorb on the surface of the catalyst and diffuse to the pores of the catalyst. Reactions occur, and products are diffused out of the pores. The products are desorbed from the catalyst surface and conveyed back to the bulk fluid. The overall reaction process is categorized into endothermic reaction where heat is consumed during the reaction or exothermic reaction where heat is generated.

In reactor modelling, it is important to understand the process occurring in the reactor and the type of reactor to be modelledhence, there is no general reactor model. Also, it is difficult to accurately describe the complex phenomena existing in the process thus;
assumptions are made to reduce the complexity of the models. Effective parameter estimation in numerical modelling is used to account and calculate each elementary process. Model selection is based on the system properties under investigation, the availability of existing data, model equations that define the system and the numerical solution approach (Lorandidis, 2002).

There are two (2) main classifications for packed bed reactor models

a. Continuum Model

Continuum fixed bed model is divided into pseudo–homogenous and heterogeneous. In this model, the observable processes may be: heat and mass diffusion in the particle, heat and mass transfer between the solid and fluid phase, fluid convection, thermal conduction of the catalyst and dispersion of heat and mass in the bulk gas (Lorandidis, 2002). There exist different set of equations for both phases (Froment and Bischoff, 1979; Lorandidis, 2002).

b. Cell Model

The cell model considers the pellet and the bulk fluid around it as a cell. This model examines the interaction between the cell unit and the adjacent cells (McGuire and Lapidus, 1965; Lorandidis, 2002). The cell type and its interaction with neighboring cells predict the transport processes (Lorandidis, 2002).

Continuum model is the most commonly used classification hence, it is easy to model numerically and verified due to the presence of large experimental data. In pseudo homogenous model, both the solid and fluid phases are assumed to exist in one pseudo phase and one equation is written for both phases whereas for the heterogeneous model,
different sets of equations are written for both the gas and liquid phase. A schematic diagram of the continuum models is shown in figure 2-5.

2.3.1 Fixed Bed Reactors.

Over the years, reactor modelling has been studied by a lot of researchers due to its significance in different processes. A review on what researchers have done pertaining to fixed bed reactor modelling is what this section seeks to describe. Other references besides the ones found in table 2-9 are Tye et al., (2002); Schlereth and Hinrichsen, (2014); Nezhad et al., (2009); Tan et al., (2008); Murmura et al., (2016); Ni (2013); Marcoberadino et al., (2015); Olayeye et al., (2014); Cao et al., (2015) and Ghasemzadeh et al., (2016). More information is found in table 2-9.

2.4 Summary

The kinetics of SR, TOR, ATR and CO₂ Methanation was reviewed based on the LHHW and ER techniques. Adsorption and surface reaction steps were mostly found to be the rate determining steps (RDS). From table 2-1, SR and POR are already commercialized whereas, ATR is a near term reforming technology with 60-75 % efficiency thus, using ATR process will serve as a significant contribution to the technology. On the other hand, fixed bed reactors are easy to design and have high conversion. The main categories are pseudo homogenous and heterogenous models. The most common software or method used are finite difference Method (FDM), COMSOL Multiphysics and gPROMS. Reactors are modelled either transient or steady state mode.
Continuum Model

Pseudo homogenous model
No explicit equation for the catalyst.
Requires effectiveness factor.
Negligible gradient between phases.
Rate of expression in terms of fluid phase temperature and concentration.

Heterogeneous

Simplified heterogeneous
Contains effectiveness factor.
Accounts explicitly for external heat and mass transfer to solid.

Conventional heterogeneous
Consider pellet equation to account for mass transport.

Figure 2-5: Continuum Fixed Bed Model (Rout and Jakobsen, 2015)
Table 2-9: Summary on literature Review on Numerical Modelling.

<table>
<thead>
<tr>
<th>Description</th>
<th>Catalyst &amp; Temperature</th>
<th>Software/Method</th>
<th>Focus/Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-D HET dynamic modelling of ATR of Methane for predicting dynamic responses with flow rate pulses;</td>
<td>Ni based 773 K</td>
<td>FDM</td>
<td>• Fixed effectiveness factor for each reaction but had variable reaction rates. • An increase or decrease in step size adversely affects CO and methane conversion.</td>
<td>Chan et al., 2005</td>
</tr>
<tr>
<td>2-D PH steady state modelling study for a PBTR. For the reforming of crude ethanol with industrial data</td>
<td>Ru based 973 k</td>
<td>COMSOL (FEM)</td>
<td>• Momentum balances should be solved for industrial scale to ensure plug flow conditions.</td>
<td>Aboudheir et al., 2006</td>
</tr>
<tr>
<td>1-D HET, dynamic modelling of ATR of Methane under small-scale conditions</td>
<td>Ni based 773 K</td>
<td>gPROMS (Backward Euler)</td>
<td>• Use of effectiveness Factors. • Optimization identified the conditions to enhance methane conversion.</td>
<td>Halabi et al., 2008</td>
</tr>
<tr>
<td>Description</td>
<td>Catalyst &amp; Temperature</td>
<td>Software/Method</td>
<td>Focus/Remarks</td>
<td>Reference</td>
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</tr>
<tr>
<td>1-D HET model for ATR of Methane</td>
<td>Rh based 623-773 K</td>
<td>FDM</td>
<td>• Model predicted methane conversion and validated against experimental results.</td>
<td>Scognamiglio, 2008</td>
</tr>
<tr>
<td>2-D pseudo HET model for SMR for lab scale</td>
<td>Ni based 873-1073 K</td>
<td>COMSOL (FEM)</td>
<td>• Concluded that radial gradients were insignificant, and the model agreed with experiments.</td>
<td>Sadooghi and Rauch, 2013</td>
</tr>
<tr>
<td>2-D Pseudo HET model for SMR with H₂S for lab scale for H₂ production</td>
<td>Ni based 1173 K</td>
<td>COMSOL (FEM)</td>
<td>• Investigated the effects of varying amount of H₂S on SMR process.</td>
<td>Sadooghi and Rauch, 2015</td>
</tr>
<tr>
<td>2-D unsteady state HET model for SR of Methane. Pseudo steady state model for pressure drop</td>
<td>Raschig rings 1023.15 K</td>
<td>gPROMS (FDM)</td>
<td>• Usage of effectiveness factor. • Validated with experimental data from literature. • Extended to multi scale (Industrial) application.</td>
<td>Ghouse and Adams, 2013</td>
</tr>
<tr>
<td>Description</td>
<td>Catalyst &amp; Temperature</td>
<td>Software/Method</td>
<td>Focus/Remarks</td>
<td>Reference</td>
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<tr>
<td>----------------------------------------------------------------------------</td>
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<td>---------------------------------------------------------------------------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Dynamic HET model for an industrial Steam Methane Reforming reactor</td>
<td>800 K</td>
<td>gPROMS (Central difference)</td>
<td>• HET model gave good prediction of temperature and conversion profiles when validated.</td>
<td>Pantaleontos et al., 2012</td>
</tr>
<tr>
<td>2-D steady state numerical Study of Methanol-Air Mixture via Steam reforming in an annulus reactor.</td>
<td>Pt catalyst</td>
<td>COMSOL Multiphysics (FEM)</td>
<td>• Shell and tube arrangement type of reactor was modelled.</td>
<td>Chein et al., 2013</td>
</tr>
<tr>
<td>Similarity between packed bed and fluidized bed</td>
<td>873 K</td>
<td>Not mentioned</td>
<td>• Significant mass transfer limitation on the membrane reactor than the packed bed.</td>
<td>Gallucci et al., 2010</td>
</tr>
<tr>
<td>Description</td>
<td>Catalyst &amp; Temperature</td>
<td>Software/Method</td>
<td>Focus/Remarks</td>
<td>Reference</td>
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<td>----------------------------------------------------------------------------</td>
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<td>-------------------------------------------------------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>membrane reactor for reforming of Methane</td>
<td></td>
<td></td>
<td>• Effects of particle diameter on conversion and temperature were studied.</td>
<td></td>
</tr>
<tr>
<td>1-D Steady state model for fuel cell applications using Ammonia</td>
<td>Ni-Pt/Al₂O₃ 833 K</td>
<td>FLUENT v6.2</td>
<td>• 1-D model gave accurate predictions when compared to an already existing 2-d model.</td>
<td>Chein et al., 2010</td>
</tr>
<tr>
<td>1-D unsteady state pseudo-homogenous model for a chemical looping combustion process using a fixed bed reactor</td>
<td>Ni-Al₂O₃ 700K</td>
<td>COMSOL Multiphysics</td>
<td>• Effect of time on oxidation and reduction processes was used for optimization of the process. • Good validation with experimental data.</td>
<td>Diglio et al., 2016</td>
</tr>
<tr>
<td>One dimensional heterogeneous model for steam methane reforming</td>
<td>NiO/α Al₂O₃ 300-700 °C</td>
<td>gPROMS</td>
<td>• Adopted kinetics from Xu and Froment. • Comparison of results with equilibrium to observe the various trends.</td>
<td>Abbas et al., 2017</td>
</tr>
<tr>
<td>Description</td>
<td>Catalyst &amp; Temperature</td>
<td>Software/Method</td>
<td>Focus/Remarks</td>
<td>Reference</td>
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</tr>
<tr>
<td>3 D finite element simulation for hydrogen storage tank</td>
<td>N/A</td>
<td>COMSOL Multiphysics</td>
<td>• Modelled an adiabatic fixed bed reactor.</td>
<td>Freni et al., 2009.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Chemical engineering module in COMSOL was used to design the metal hydride-based hydrogen storage tank. Great flexibility in optimizing the tank design.</td>
<td>Muthukumar et al., 2012</td>
</tr>
<tr>
<td>1-D heterogeneous model for ATR process</td>
<td>Ni/Mg-Al₂O₃</td>
<td>TR-BDF Method</td>
<td>• Two different kinetic models were developed. One for SR and the other for POX.</td>
<td>Nezhad et al., 2009</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Increasing temperature increased reaction rate and slowed down equilibrium. Less side reactions occurred and the</td>
<td></td>
</tr>
<tr>
<td>Description</td>
<td>Catalyst &amp; Temperature</td>
<td>Software/Method</td>
<td>Focus/Remarks</td>
<td>Reference</td>
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<td>-------------------------------------------------------</td>
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</tr>
<tr>
<td>1-D HET model of autothermal reforming of methane via fixed bed reactor.</td>
<td>Rh Catalyst</td>
<td>Mathematica</td>
<td>• Adopted kinetics from literature for numerical modelling.</td>
<td>Scognamiglio et al., 2012</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Good comparison for the numerical temperature and conversion with experimental ones.</td>
<td></td>
</tr>
<tr>
<td>Modelled a monolith reactor of a fuel surrogate</td>
<td>N/A</td>
<td>Fluent 6.3.26</td>
<td>• A limitation of the work was not considering the thermal cracking of other hydrocarbons. Smaller hydrocarbons could be formed by thermal cracking to produce more reactive species and given better conversion.</td>
<td>Shi et al., 2009</td>
</tr>
<tr>
<td>Description</td>
<td>Catalyst &amp; Temperature</td>
<td>Software/Method</td>
<td>Focus/Remarks</td>
<td>Reference</td>
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</tr>
<tr>
<td>Time dependent two (2) dimensional PH and HET models</td>
<td>793-1048 K</td>
<td>MATLAB LS-SEM</td>
<td>• However, the model gave good comparison with experimental work. • Modeled both simplified and conventional HET. • Studied the effects of several diffusion models on the mole fractions of species. • Conventional HET predicted the outlet concentration and temperature well.</td>
<td>Rout and Jakobsen, 2015</td>
</tr>
</tbody>
</table>
2.5 Identified Challenges

To optimize and design any chemical process, there is the need to comprehend the reaction kinetics (Peeri.org, 2019). A reaction mechanism provides in-depth explanation on how the reaction proceeds and this is very useful in reactor design. Ghani et al., 2017 proposed a general power law model that describes the overall autothermal reforming. To gain full insight on the kinetics, series of elementary reactions were proposed to describe exactly what occurs in the ATR system. The individual reactions were analyzed and based on that, the obtained kinetics was used in reactor modelling of the ATR system. Also, there exists several literatures of autothermal reforming (ATR) using methane with a few on glycerol. Most of the available literature on the ATR process assumes complete utilization of oxygen which reduces the ATR process to steam reforming and water gas shift reaction.

In this work, the mechanistic kinetics for an in-house crude glycerol blend via ATR process is studied where the individual reactions are holistically analyzed. To the best of our knowledge, the mechanistic kinetic study for this blend of crude glycerol has not been studied in literature thus, making this current work novel.
Chapter 3: Kinetic Model Development

3.1 Experimental Summary

The experiment was conducted by Ghani et al., (2017) with a crude glycerol composition of free glycerol (45.6 %), Methanol (11.2 %), Water (8.3 %), soap (29.1 %), Oleic acid (3.8 %), Sodium and Potassium Chloride (1 % each). The catalyst (Ni/CeZrCa) was prepared via impregnation technique of Ni (5 %). According to Adhikari et al. (2006), the acceptable amount of pure glycerol present in a crude glycerol mixture for hydrogen production should be 40-80 mol %. This indicates that the prepared in-house blend of crude glycerol is viable for hydrogen production.

The experiment was conducted in a fixed bed reactor with reaction zone dimensions of 12.7 mm by 45 mm. This section is filled with the spherical Ni/CeZrCa catalyst. There was a thermocouple in the reactor for measuring the temperature of the reaction with the whole reactor embedded in a thick layer of insulation to prevent heat loss.

Based on the pre-determined Steam to Carbon ratio (S/C) and Oxygen to Carbon ratio (O_2/C), the rightful composition of steam and air (O_2=21 % and N_2=79 %) were used to provide the right autothermal conditions. The Steam was mixed with crude glycerol in predetermined quantities and introduced into the reactor via a syringe pump. Concurrently, air was also introduced into the reactor and the reactants were left in the reactor where the ATR reactions occurred. The exit gas was passed through a condenser to cool it and the condensate was collected. Finally, the gas was sent to the Gas chromatography for analysis.
3.2 Plug Flow Conditions

Before the kinetics of crude glycerol autothermal system was studied, kinetic analysis was performed to ensure the absence of heat and mass transfer limitation. According to Froment and Bischoff (1990), and Rase (1987), the criteria to ensure plug flow conditions and the absence of back mixing was also tested. According to Ibrahim et al. (2006), the occurrence of transport resistances (heat and mass) occurred at the peak temperature (923 K) which enabled us to use this value for the kinetic analysis.

- Bed height to particle size ratio
  \[
  \frac{L}{d_p} \geq 50 \quad (3.1)
  \]
  Where \( L \) is the length of the reactor and \( d_p \) the diameter of the catalyst particle
  For this work, \( 56.25 \geq 50 \) thus this condition was fulfilled

- Internal diameter to the catalyst size ratio
  \[
  \frac{D}{d_p} \geq 10 \quad (3.2)
  \]
  Where \( D \) is the diameter of the reactor and \( d_p \) the diameter of the catalyst particle
  For this work, \( 15.88 \geq 10 \) thus this condition was also fulfilled.
3.3 Heat Transfer Limitation

For heat transfer limitation condition, internal heat transfer limitation condition as provided by the Prater analysis was used. This considered the heat transfer from the core of the catalyst pellet to the surface. External heat transfer limitation condition was for heat transfer from the bulk gas mixture to surface of the catalyst. A stern analysis called Mears criteria was used to finalize the conclusion of heat transfer limitation. The various analyses are as summarized below:

• Internal Heat transfer

The formula used to analyze the Prater criteria is given by

$$\Delta T_{\text{max,particle}} = \frac{D_{\text{eff}}(C_{AO} - C_{AI})\Delta H_r}{\lambda_{\text{eff}}} < 1 \quad (3.3)$$

$D_{\text{eff}}$ is the effective diffusivity which is calculated based on correlation from Fogler (1990); $C_{AO}$ and $C_{AI}$ are the inlet and exit concentration respectively; $\Delta H_r$ is the heat of reaction and $\lambda_{\text{eff}}$ is the thermal conductivity coefficient. From the interpretation, $\Delta T_{\text{max,particle}}$ was found to be 0.15K which denotes an even temperature within the catalyst pellet.

• External Heat Transfer

The formula for the inter particle heat transfer is given by

$$\Delta T_{\text{max,film}} = \frac{L_c(r_{\text{obs}})\Delta H_r}{h} < 1 \quad (3.4)$$

This criterion is for heat transfer between the surface of the pellet (the gas film) and the bulk gas. $L_c$ is the characteristic length, $r_{\text{obs}}$ is the observed rate, $h$ is the heat transfer coefficient and $H_r$ is the heat of reaction. $\Delta T_{\text{max,film}}$ was calculated as 0.6. It can be
deduced from this value that, there is no significant change in temperature difference between the gas film and the bulk gas. Levenspiel (1999) supports the assumption of heat transfer from the catalyst surface to the bulk gas.

- Mears Criterion

Mears criterion (Mears, 1971) which gives a much stern analysis was finally used to conclude on the heat transfer analysis for both internal and external heat transport. The correlation is given as;

\[
r_{\text{obs}} \rho g R_c E_a \Delta H_r < 0.15
\]

\[\frac{r_{\text{obs}} \rho g R_c E_a \Delta H_r}{hT^2 R} < 0.15 \tag{3.5}\]

\(r_{\text{obs}}\) is the observed rate, \(h\) is the heat transfer coefficient and \(H_r\) is the heat of reaction, \(T\) is the reaction temperature, \(R_c\) is the radius of the pellet, \(E_a\) is the activation energy and \(R\) is the universal gas constant. After computations, the left-hand side of the equation yielded 0.02 which is far less than 0.15. Therefore, the system has no heat transfer limitations.

### 3.4 Mass Transfer Limitation

Mass transfer limitation criteria follow the same concept of the heat transfer limitation.

- Internal Pore Mass Transfer Resistance using Weisz Prater

\[
C_{wp} = \frac{-r_{\text{obs}} \rho_c R_c^2}{D_{eff} C_{A_0}} < 1 \tag{3.6}
\]

\(r_{\text{obs}}\) is the observed rate, \(C_{A_0}\) is the exit concentration and \(\rho_c\) is the density of the catalyst pellet, \(R_c\) is the radius of the pellet, \(D_{eff}\) is the effective diffusivity. The Weisz Prater criterion yielded 0.24 which is less than 1. As stated by Fogler (1999), since this numerical
value is less than 1, there is no concentration gradient within the pellet and thus, no limitations to internal pore diffusion.

- **Mass Transfer across Film**

Mass transfer across the film is also termed external mass transfer. The formula is as shown below

\[
\frac{\text{observed rate}}{\text{rate if film transfer resistance controls}} = \frac{-r_{\text{obs}} d_p}{C_{A,o} k_c 6}
\]  

(3.7)

\(r_{\text{obs}}\) is the observed rate, \(C_{A,o}\) is the exit concentration and \(k_c\) is the mass transfer coefficient and \(d_p\) is the diameter of the pellet? The right-hand side after computation gave \(6.9 \times 10^{-3}\) and it could be concluded that the observed rate is much smaller than the ‘rate obtained if film transfer controls. Thus, the rate due to film transfer resistance does not limit the rate of reaction (Levenspiel, 1999).

- **Mears’ Criterion**

\[
\frac{-r_{\text{obs}} \rho_g R_c n}{C_{A,o} k_c} < 0.15
\]  

(3.8)

A strict criterion used to buttress the observation made above. The parameters in the above formulation is \(r_{\text{obs}}\) for the observed rate; \(C_{A,o}\) is the exit concentration; \(k_c\) is the mass transfer coefficient; \(R_c\) is the radius of the pellet; \(\rho_g\) is the density of the bulk gas and \(n\) is the overall order of reaction. The value of 0.072 was obtained which is less than 0.15 thus, giving a conclusion that there was no mass transfer limitation during the kinetic data collection (Levenspiel, 1999; Mears,1971 & Fogler, 1999).
3.5 Independent Reactions

Ghani et al., (2017) came up with an empirical formula for crude glycerol \((C_{2.5}H_7O_2)\). Hence, the overall equation used to represent this system is given as:

\[
C_{2.5}H_7O_2 + 0.7 H_2O + 0.65 O_2 \rightarrow 2CO_2 + 0.5 CH_4 + 3.2 H_2 \quad \Delta H_{298K} = -72.39 \frac{KJ}{mol}
\]  
(3.9)

According to Ghani et al. (2017), a typical autothermal reaction is composed of steam reforming reaction, partial oxidation reaction and other side reactions (methanation reaction, methane dry reforming, glycerol decomposition, coke formation and others).

Some of the reactions are as shown below:

1. Steam reforming
   
   \[
   C_3H_8O_3 + 3 H_2O \rightarrow 3CO_2 + 7 H_2 \quad \Delta H_{298K} = +127.7 \frac{KJ}{mol}
   \]  
   (3.10)

2. Partial and total Oxidation
   
   \[
   C_3H_8O_3 + 1.5 O_2 \rightarrow 3 CO_2 + 4 H_2 \quad \Delta H_{298K} = -597.7 \frac{KJ}{mol}
   \]  
   (3.11 a)

   \[
   C_3H_8O_3 + 2 O_2 \rightarrow 3 CO + 4 H_2O \quad \Delta H_{298K} = -715.9 \frac{KJ}{mol}
   \]  
   (3.11 b)

3. Methanation Reaction
   
   \[
   CO + 3 H_2 \rightarrow CH_4 + H_2O \quad \Delta H_{298K} = -206.2 \frac{KJ}{mol}
   \]  
   (3.12)

4. Methane Dry Reforming
   
   \[
   CO_2 + CH_4 \rightarrow 2 H_2 + 2 CO \quad \Delta H_{298K} = -247.4 \frac{KJ}{mol}
   \]  
   (3.13)

5. Water Gas Shift Reaction
   
   \[
   CO + H_2O \rightarrow H_2 + CO_2 \quad \Delta H_{298K} = -41.8 \frac{KJ}{mol}
   \]  
   (3.14)
Lots of reactions occur for autothermal reforming of hydrocarbon and as such, it is prudent to know which exact reactions define the system. As stated by Liu and Lawal (2015), a matrix approach is used to obtain the rank of the matrix which indicates the number of independent reactions that describes the system under studies. The species \((C_3H_8O_3, H_2, CO_2, H_2O, CH_4, O_2)\) for the crude glycerol autothermal reforming system were basically C, H, O on atomic basis.

Number of independent reactions = Number of columns - Rank of Matrix

Using MATLAB 2017a, this six (6) column table has a rank of three (3) and the total number of independent reactions is 3.

Based on the final equation proposed by Ghani et al., 2017 and the GC analysis, it could be inferred that the three (3) main reactions are:

- Steam Reforming
- Total Oxidation Reaction (since there was no formation of carbon monoxide (CO)).
- Carbon dioxide (CO\(_2\)) (Methanation due to the presence of methane in the product stream).

### 3.6 Power Law Model

The power law is a rate law expression written in terms of reactants and/or products. It considers the reversibility and irreversibility of the reaction. Assuming the overall reaction is an elementary reaction, the rate law given by the power law expression is given in terms of the stoichiometric coefficient.
\[ C_{2.5}H_7O_2 + 0.7 H_2O + 0.65 O_2 \rightarrow 2CO_2 + 0.5 CH_4 + 3.2 H_2 \Delta H^{298K} = -72.39 \frac{kJ}{mol} \]  

(3.15)

- **Reversible Reaction**

The reaction is written in terms of the reactants and products. This reaction considers both the forward and reverse reactions. The rate law expression is as follows;

\[
r = k_0r e^{-\left(\frac{E_f}{RT}\right)p_{CG}^m p_{H_2O}^n p_{H_2O}^o} - k_0r e^{-\left(\frac{E_r}{RT}\right)p_{CO_2}^q p_{CH_4}^r p_{H_2}^s} \tag{3.16}
\]

- **Irreversible**

The reaction is written in terms of only reactants which present the forward rate. The rate law expression is given as;

\[
r = k_0f e^{-\left(\frac{E_f}{RT}\right)p_{CG}^m p_{H_2O}^n p_{H_2O}^o} \tag{3.17}
\]

**3.7 Mechanistic Model Development**

Autothermal Reforming of crude glycerol was subdivided into three (3) independent reactions, the kinetics studied and analyzed for each reaction (Liu and Lawal, 2015). The mechanistic models obtained were derived based on, Eley-Rideal (ER) and Langmuir Hinshelwood Hougen Watson (LHHW). For the sake of simplicity, crude glycerol was written out as pure glycerol in which both reversible and irreversible mechanistic and power law models were derived.

The overall reaction was given by;

\[ C_{2.5}H_7O_2 + 0.7 H_2O + 0.65 O_2 \rightarrow 2CO_2 + 0.5 CH_4 + 3.2 H_2 \]  

(3.18)

- **Steam Reforming**
0.8 \text{C}_2\text{H}_7\text{O}_2 + 2.4 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 5.2 \text{H}_2 \quad (3.19)

- Oxidation

0.2 \text{C}_2\text{H}_7\text{O}_2 + 0.65 \text{O}_2 \rightarrow 0.5 \text{CO}_2 + 0.7 \text{H}_2\text{O} \quad (3.20)

- Methanation

0.5 \text{CO}_2 + 2 \text{H}_2 \rightarrow 0.5 \text{CH}_4 + \text{H}_2\text{O} \quad (3.21)

### 3.7.1 Steam Reforming Reaction (SR)

Steam reforming reaction occurs when steam reacts with the crude glycerol to form carbon dioxide (\text{CO}_2) and hydrogen gas (\text{H}_2). The reaction for SR is given by:

\[
0.8 \text{A} + 2.4 \text{B} \leftrightarrow 2 \text{E} + 5.2 \text{F} \quad (3.22)
\]

According to Vaidya et al. (2012) and Adesina et al. (2011), a plausible mechanism for glycerol steam reforming normally has dehydrogenation, scission of C-C and C-O bonds as well as dehydration and hydration steps.

1. **Eley-Rideal Approach:** Steam reforming did not produce methane as products and the assumption that reactant(s) adsorption and products desorption from catalyst active site is considered in site balance. Vacant active sites were also accounted for in the site balance.

   - Molecular Adsorption of crude glycerol on active site

   \[
   0.8 \text{A} + 2\text{S} \rightarrow \text{A.S} + \text{S} \quad (3.23)
   \]

   - Dissociation of adsorbed intermediate on a vacant site to form two (2) different oxygenated hydrocarbon compounds (ethylene glycol and formaldehyde).

   \[
   \text{A.S} + \text{S} \rightarrow \text{H.S} + \text{I.S} \quad (3.24)
   \]
• Surface Reaction between adsorbed intermediate and non-adsorbed steam in the bulk gas

\[ \text{H.S} + 2.2 \text{ B} \rightarrow 1.5 \text{ E} + 4.2 \text{ F} + \text{S} \]  \hspace{1cm} (3.25)

\[ \text{I.S} + 0.2 \text{ B} \rightarrow 0.5 \text{ E} + \text{ F} + \text{S} \]  \hspace{1cm} (3.26)

2. Langmuir Hinshelwood Method

Here, the assumption is made that both crude glycerol and water (steam) were both adsorbed on the catalyst active site. An approach like Adesina et al. (2010) was modified where both molecular and atomic adsorption of the reactants were considered to give a better understanding of the mechanism.

Molecular adsorption of crude glycerol on active site

\[ 0.8 \text{ A} + \text{ S} \rightarrow 0.8 \text{ A.S} \]  \hspace{1cm} (3.27)

• Molecular adsorption of steam on active site

\[ 2.4 \text{ B} + \text{ S} \rightarrow 2.4 \text{ B.S} \]  \hspace{1cm} (3.28)

• Surface reaction between adsorbed intermediate for both crude glycerol and water

\[ 0.8 \text{ A.S} + 2.4 \text{ B.S} \rightarrow \text{G.S} + \text{ S} \]  \hspace{1cm} (3.29)

• Desorption of products from active site

\[ \text{G.S} \rightarrow 2 \text{ E} + 5.2 \text{ F} + \text{S} \]  \hspace{1cm} (3.30)
Table 3-1: Matrix Ranking Approach

<table>
<thead>
<tr>
<th>Atom</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>H_2</td>
<td>CO_2</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
</tr>
<tr>
<td>H</td>
<td>2</td>
</tr>
<tr>
<td>O</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3-2: Summary of rate equation assuming each step as a rate determining step assuming both reversible and irreversible reactions.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Rate Law Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER_1</td>
<td>( r_1 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{([A]^{0.8} - \frac{[E]^2[F]^{5.2}}{K_{p(eq)}([B])^{2.4}})}{1 + \frac{K_F[E]^2[F]^{5.2}}{([B])^{2.4}} + \frac{K_B[E][F]^{1.5}[F]^{4.2}}{([B])^{2.2}} + \frac{K_A[E][F]^{0.5}}{([B])^{0.2}}} \right] )</td>
</tr>
<tr>
<td>ER_2</td>
<td>( r_2 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{([A]^{0.8} - \frac{[E]^2[F]^{5.2}}{K_{p(eq)}([B])^{2.4}})}{1 + K_A[A]^{0.8} + \frac{K_B[F][E]^{0.5}}{([B])^{0.2}} + \frac{K_W[E][F]^{1.5}[F]^{4.2}}{([B])^{2.2}}} \right] )</td>
</tr>
<tr>
<td>ER_3</td>
<td>( r_3 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{([A]^{0.8}[B]^{2.4}}{([F][E]^{0.5} - \frac{[E]^{1.5}[F]^{4.2}}{K_{p(eq)}})}{1 + K_1[A]^{0.8} + \frac{K_W[A][F]^{0.8}[B]^{0.2}}{([F][E]^{0.5} + \frac{K_B[E][F]^{0.5}}{([B])^{0.2}}} \right] )</td>
</tr>
<tr>
<td>ER_4</td>
<td>( r_4 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{([A]^{0.8}[B]^{2.4}}{([E]^{1.5}[F]^{4.2} - \frac{[F][E]^{0.5}}{K_{p(eq)}})}{1 + K_1[A]^{0.8} + \frac{K_W[A][F]^{0.8}[B]^{2.2}}{([E]^{1.5}[F]^{4.2} + \frac{K_C[E][F]^{1.5}[F]^{4.2}}{([B])^{2.2}}} \right] )</td>
</tr>
<tr>
<td>ER_5</td>
<td>( r_5 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{([A]^{0.8}}{1 + \frac{K_F[E]^2[F]^{5.2}}{([B])^{2.4}} + \frac{K_B[E][F]^{1.5}[F]^{4.2}}{([B])^{2.2}} + \frac{K_A[E][F]^{0.5}}{([B])^{0.2}}} \right] )</td>
</tr>
<tr>
<td>Equation</td>
<td>Rate Law Expression</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------</td>
</tr>
<tr>
<td>ER_6</td>
<td>$r_6=k_0e^{-\left(\frac{E_a}{RT}\right)} \times \frac{([A]^{0.8})}{\left[1 + K_A[A]^{0.8} + \frac{K_B[E]^{0.5}[F]}{([B]^{0.2})} + \frac{K_W[E]^{1.5}[F]^{4.2}}{([B]^{2.2})}\right]}$</td>
</tr>
<tr>
<td>ER_7</td>
<td>$r_7=k_0e^{-\left(\frac{E_a}{RT}\right)} \times \frac{([A]^{0.8}[B]^{2.4})}{\left(1 + K_A[A]^{0.8} + \frac{K_W[A]^{0.8}[B]^{0.2}}{[E]^{0.5}[F]} + \frac{K_B[E]^{0.5}[F]}{[B]^{0.2}}\right)}$</td>
</tr>
<tr>
<td>ER_8</td>
<td>$r_8=k_0e^{-\left(\frac{E_a}{RT}\right)} \times \frac{([A]^{0.8}[B]^{2.4})}{\left(1 + K_A[A]^{0.8} + \frac{K_W[A]^{0.8}[B]^{2.2}}{[E]^{1.5}[F]^{4.2}} + \frac{K_B[E]^{1.5}[F]^{4.2}}{[B]^{2.2}}\right)}$</td>
</tr>
<tr>
<td>LHHW_1</td>
<td>$r_1=k_0e^{-\left(\frac{E_a}{RT}\right)} \times \frac{([A]^{0.8} - \frac{[E]^{2}[F]^{5.2}}{K_p(eq)([B]^{2.4})})}{\left(1 + K_2[B]^{2.4} + K_B[E]^{2}[F]^{5.2} + \frac{K_W[E]^{2}[F]^{5.2}}{([B]^{2.4})}\right)}$</td>
</tr>
<tr>
<td>LHHW_2</td>
<td>$r_2=k_0e^{-\left(\frac{E_a}{RT}\right)} \times \frac{([B]^{2.4} - \frac{[E]^{2}[F]^{5.2}}{K_p(eq)([A]^{0.8})})}{\left(1 + K_1[A]^{0.8} + K_B[E]^{2}[F]^{5.2} + \frac{K_W[E]^{2}[F]^{5.2}}{([A]^{0.8})}\right)}$</td>
</tr>
<tr>
<td>LHHW_3</td>
<td>$r_3=k_0e^{-\left(\frac{E_a}{RT}\right)} \times \frac{([A]^{0.8}[B]^{2.4} - \frac{[E]^{2}[F]^{5.2}}{K_p(eq)})}{\left(1 + K_1[A]^{0.8} + K_B[E]^{2}[F]^{5.2} + K_2[B]^{2.4}\right)^2}$</td>
</tr>
<tr>
<td>LHHW_4</td>
<td>$r_4=k_0e^{-\left(\frac{E_a}{RT}\right)} \times \frac{([A]^{0.8}[B]^{2.4} - \frac{[E]^{2}[F]^{5.2}}{K_p(eq)})}{\left(1 + K_1[A]^{0.8} + K_B[A]^{0.8}[B]^{2.4} + K_2[B]^{2.4}\right)}$</td>
</tr>
</tbody>
</table>

** A=C₃H₅O₃; B=H₂O; C=O₂; D=CH₄; E=CO₂, H=C₂H₆O₂; I=CH₂O; G =CH₃(CH₂)ₓCOOH **
3.7.2 Oxidative Reforming (TOR)

Oxidation reactions can be categorized into either total oxidation or partial oxidation. For partial oxidation, the obtained products are CO and H₂ (Hu and Ruckenstein, (1996); Dinh et al., (2017); Ibrahim and Idem, (2006); Oluku et al., (2018); Adhikari et al., (2007)) whereas for total oxidation, the products formed are CO₂ and H₂O (Shi et al., (2009); Hohn and Lin, (2009); Beretta et al., (2009); Leclerc, (2007)). In this work, crude glycerol is reacted with Oxygen to produce carbon dioxide (CO₂) and water (H₂O). The reaction is highly exothermic and is given by:

\[ 0.2 \text{C}_2\text{H}_5\text{O}_2 + 0.65 \text{O}_2 \rightarrow 0.5 \text{CO}_2 + 0.7 \text{H}_2\text{O} \]  \hspace{1cm} (3.31)

For the mechanistic model, both LHHW and Eley Rideal models were considered.

- Eley Rideal: Oxygen was assumed to be adsorbed on the active site catalyst whilst the crude glycerol existed in the bulk gas phase. This model was based on a single site mechanism.

  (a) Molecular adsorption of oxygen on an active site

\[ 0.65 \text{C} + \text{S} \rightarrow 0.65 \text{C. S} \]  \hspace{1cm} (3.32)

- Surface reaction of adsorbed Oxygen and non-adsorbed crude glycerol

\[ 0.2 \text{A} + 0.65 \text{C}.\text{S} \rightarrow \text{W. S} \]  \hspace{1cm} (3.33)

- Molecular desorption of intermediate

\[ \text{W. S} \rightarrow 0.5 \text{E} + 0.7 \text{B} + \text{S} \]  \hspace{1cm} (3.34)

(b) Dissociative adsorption of oxygen on an active site

\[ 0.65 \text{C} + \text{S} \rightarrow 1.3 \text{C}.\text{S} \]  \hspace{1cm} (3.35)
• Surface reaction of adsorbed Oxygen and non-adsorbed crude glycerol

\[0.2 \ A + 0.3 \ C.S \rightarrow V.S\] \hspace{1cm} (3.36)

• Surface reaction of adsorbed intermediate with the remaining Oxygen

\[V.S + C.S \rightarrow W.S + S\] \hspace{1cm} (3.37)

• Desorption of active intermediate from active site

\[W.S \rightarrow 0.5 \ E + 0.7 \ B + S\] \hspace{1cm} (3.38)

• Langmuir Hinshelwood

Oxygen and crude glycerol are both adsorbed on the active sites. The elementary steps for this mechanism is as described below:

• Dissociative adsorption of oxygen on an active site

\[0.65 \ C + S \rightarrow 1.3 \ C.S\] \hspace{1cm} (3.39)

• Non-dissociative adsorption of crude glycerol on an active site

\[0.2 \ A + S \rightarrow 0.2 \ A.S\] \hspace{1cm} (3.40)

• Surface reaction of adsorbed intermediates

\[0.2 \ A. S + 1.3 \ C. S \rightarrow 0.5 E.S + 0.7 B.S\] \hspace{1cm} (3.41 a)

\[0.2 \ A. S + 1.3 \ C. S \rightarrow W. S + S\] \hspace{1cm} (3.41 b)

• Desorption of adsorbed intermediate

\[W.S \rightarrow 0.5 \ E.S + 0.7 \ B\] \hspace{1cm} (3.42)

\[0.5 \ E.S \rightarrow 0.5 \ E + S\] \hspace{1cm} (3.43)
Table 3-3: Rate law expression for Eley Rideal Model via Oxidation Reforming Route.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Rate Law Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER_1</td>
<td>( r_1 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[C]^{0.65} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)[A]^{0.2}}}{1 + K_A[E]^{0.5}[B]^{0.7} + K_B[E]^{0.5}[B]^{0.7}} \right] )</td>
</tr>
<tr>
<td>ER_2</td>
<td>( r_2 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[A]^{0.2}[B]^{0.65} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)}\right]{1 + K_B[E]^{0.5}[B]^{0.7} + K_A[C]^{0.65}} )</td>
</tr>
<tr>
<td>ER_3</td>
<td>( r_3 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[A]^{0.2}[B]^{0.65} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)}\right]{1 + K_2[C]^{0.65} + K_A[A]^{0.2}[C]^{0.65}} )</td>
</tr>
</tbody>
</table>

Rate law expression for Eley Rideal Model via Oxidation route (Dissociative adsorption of Oxygen)

<table>
<thead>
<tr>
<th>Equation</th>
<th>Rate Law Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER_4</td>
<td>( r_4 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[C]^{0.65} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)[A]^{0.2}}}{1 + K_C[E]^{0.5}[B]^{0.7} + K_B[E]^{0.5}[B]^{0.7}}\right] )</td>
</tr>
<tr>
<td>ER_5</td>
<td>( r_5 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[A]^{0.2}[C]^{0.65} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)[C]^{0.7.3}}}{1 + K_3[C]^{0.65} + K_B[E]^{0.5}[B]^{0.7} + K_C[E]^{0.5}[B]^{0.7}}\right] )</td>
</tr>
<tr>
<td>ER_6</td>
<td>( r_6 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[A]^{0.2}[C]^{0.65} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)}}{1 + K_3[C]^{0.65} + K_B[E]^{0.5}[B]^{0.7} + K_C[E]^{0.5}[B]^{0.7}}\right] )</td>
</tr>
<tr>
<td>ER_7</td>
<td>( r_7 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[A]^{0.2}[C]^{0.65} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)}}{1 + K_3[C]^{0.65} + K_B[E]^{0.5}[B]^{0.7} + K_C[E]^{0.5}[B]^{0.7}}\right] )</td>
</tr>
<tr>
<td>LHHW_1</td>
<td>( r_1 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[C]^{0.65} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)[A]^{0.2}}}{1 + K_6[E]^{0.5} + K_1[A]^{0.2} + K_B[E]^{0.5}[B]^{0.7} + K_C[E]^{0.5}[B]^{0.7}}\right] )</td>
</tr>
<tr>
<td>LHHW_2</td>
<td>( r_2 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[A]^{0.2} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)[C]^{0.65}}}{1 + K_3[C]^{0.65} + K_2[E]^{0.5} + K_B[E]^{0.5} + K_C[E]^{0.5}[B]^{0.7}}\right] )</td>
</tr>
<tr>
<td>LHHW_2a</td>
<td>( r_2 = k_0 e^{-\frac{E_a}{RT}} \times \left[ \frac{[A]^{0.2} - \frac{[E]^{0.5}[B]^{0.7}}{K_p(eq)[C]^{0.65}}}{1 + K_3[C]^{0.65} + K_2[E]^{0.5} + K_B[E]^{0.5} + K_C[E]^{0.5}[B]^{0.7}}\right] )</td>
</tr>
<tr>
<td>Equation</td>
<td>Rate Law Expression</td>
</tr>
<tr>
<td>----------</td>
<td>---------------------</td>
</tr>
<tr>
<td>LHHW_3</td>
<td>$r_3 = k_0 e^{-\left(\frac{E_a}{RT}\right)} \times \left[ \frac{(A)^{0.2}(C)^{0.65} - (E)^{0.5}}{(K_p(eq) - (1 + K_3[C]^{0.65} + K_1[A]^{0.2} + K_6[E]^{0.5} + K_B[E]^{0.5}[B]^{0.7}))} \right]$</td>
</tr>
<tr>
<td>LHHW_4</td>
<td>$r_4 = k_0 e^{-\left(\frac{E_a}{RT}\right)} \times \left[ \frac{(A)^{0.2}(C)^{0.65} - (E)^{0.5}}{(K_p(eq) - (1 + K_3[C]^{0.65} + K_1[A]^{0.2} + K_6[E]^{0.5} + K_B[E]^{0.5}[B]^{0.7})^2)} \right]$</td>
</tr>
<tr>
<td>LHHW_5</td>
<td>$r_5 = k_0 e^{-\left(\frac{E_a}{RT}\right)} \times \left[ \frac{(A)^{0.2}(C)^{0.65} - (E)^{0.5}}{(K_p(eq) - (1 + K_3[C]^{0.65} + K_1[A]^{0.2} + K_B[A]^{0.2} + K_6[C]^{0.65} + K_F[A]^{0.2}(C)^{0.65})^{0.7}} \right]$</td>
</tr>
<tr>
<td>LHHW_6</td>
<td>$r_6 = k_0 e^{-\left(\frac{E_a}{RT}\right)} \times \left[ \frac{(K_1 K_2[A][B])}{(1 + (K_1[B]) + (K_2[A]))^2)} \right]$</td>
</tr>
<tr>
<td>LHHW_7</td>
<td>$r_7 = k_0 e^{-\left(\frac{E_a}{RT}\right)} \times \left[ \frac{(K_1 K_2[A]^{0.2}[B]^{0.65}) - (c^{0.5}p^{0.7})}{(1 + (K_1[B]^{0.65}) + (K_2[A]^{0.2})^3)} \right]$</td>
</tr>
</tbody>
</table>

Based on Huang et al. (2012) using a reversible reaction and the stoichiometry equation as an elementary reaction

** A=C\textsubscript{3}H\textsubscript{8}O\textsubscript{3}; B=H\textsubscript{2}O; C=O\textsubscript{2}; D=CH\textsubscript{4}; E=CO\textsubscript{2}; W=CH\textsubscript{2}O\textsubscript{2}; V=CH\textsubscript{2}O; S=active site**
3.7.3 Carbon dioxide (CO2) Methanation

Carbon dioxide (CO$_2$) methanation reaction occurs between carbon dioxide and hydrogen gas to form methane gas and steam. In this work, this reaction formed methane (CH$_4$) which is an undesired product. This reaction is exothermic, and the reaction is given by:

$$0.5 \text{CO}_2 + 2 \text{H}_2 \rightarrow 0.5 \text{CH}_4 + \text{H}_2O$$

The reaction models considered were both power law and mechanistic models. For the power law model, an assumption of an irreversible reaction yielded very high AAD for the reaction. As such, a formulation like Koschany et al., (2016) was adopted which gave a better absolute average deviation (AAD) than the power law by Arrhenius. This formulation assumed a reversible reaction for the CO$_2$ methanation reaction. Other models from literature were fitted to the experimental data but gave no convergence hence, they were discarded. Extra information on CO$_2$ Methanation is available in Rogeria, 2016.

1. Eley-Rideal Model

This model was categorized into two (2) based on the assumption that either carbon dioxide or Hydrogen was first adsorbed on the active site.

- Adsorption of carbon dioxide on a site

$$0.5 \text{E} + \text{S} \rightarrow 0.5 \text{E} \cdot \text{S}$$

- Adsorption of hydrogen gas on an active site

$$2 \text{F} + \text{S} \rightarrow 2\text{F} \cdot \text{S}$$

- Surface reaction between adsorbed carbon dioxide and hydrogen gas

$$0.5 \text{E} \cdot \text{S} + 2 \text{F} \rightarrow \text{Z} \cdot \text{S}$$

- Desorption of intermediate from the active site

$$\text{Z} \cdot \text{S} \rightarrow 0.5 \text{D} + \text{B} + \text{S}$$
Table 3-4: Summary of Rate Law Expression for CO\textsubscript{2} Methanation.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Rate Law Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER_1</td>
<td>$r_1 = k_0 e^{-\frac{E_a}{RT}} \times \left( \frac{[E]^{0.5} - [D]^{0.5}[B]}{K_{p(eq)}[F]} \right) \times \left(1 + K_{3(ads)}[D]^{0.5}[B] + \frac{K_{1(ads)}[D]^{0.5}[B]}{([F]^2)} \right)$</td>
</tr>
<tr>
<td>ER_2</td>
<td>$r_2 = k_0 e^{-\frac{E_a}{RT}} \times \left( \frac{[E]^{0.5}[F]^2 - [D]^{0.5}[B]}{K_{p2(eq)}} \right) \times \left(1 + K_{1(ads)}[E]^{0.5} + K_{3(ads)}[D]^{0.5}[B]) \right)$</td>
</tr>
<tr>
<td>ER_3</td>
<td>$r_3 = k_0 e^{-\frac{E_a}{RT}} \times \left( \frac{[E]^{0.5}[F]^2 - [D]^{0.5}[B]}{K_{p2(eq)}} \right) \times \left(1 + K_{1(ads)}[E]^{0.5} + K_{3(ads)}[E]^{0.5}[F]) \right)$</td>
</tr>
</tbody>
</table>

Summary of Rate Law Expression for H\textsubscript{2} adsorption on active site

<table>
<thead>
<tr>
<th>Equation</th>
<th>Rate Law Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER_4</td>
<td>$r_4 = k_0 e^{-\frac{E_a}{RT}} \times \left( \frac{[F]^2 - [D]^{0.5}[B]}{K_{p(eq)}[E]^{0.5}} \right) \times \left(1 + K_{3(ads)}[D]^{0.5}[B] + \frac{K_{1(ads)}[D]^{0.5}[B]}{([E]^{0.5})} \right)$</td>
</tr>
<tr>
<td>ER_5</td>
<td>$r_5 = k_0 e^{-\frac{E_a}{RT}} \times \left( \frac{[E]^{0.5}[F]^2 - [D]^{0.5}[B]}{K_{p(eq)}[H_2]^2 + K_{3(ads)}[D]^{0.5}[B])} \right)$</td>
</tr>
<tr>
<td>ER_6</td>
<td>$r_6 = k_0 e^{-\frac{E_a}{RT}} \times \left( \frac{[E]^{0.5}[F]^2 - [D]^{0.5}[B]}{K_{p(eq)}[F]^2 + K_{3(ads)}[D]^{0.5}[F]^2)} \right)$</td>
</tr>
<tr>
<td>Model</td>
<td>Rate Law Expression</td>
</tr>
<tr>
<td>-------</td>
<td>---------------------</td>
</tr>
<tr>
<td>M1</td>
<td>( r = k_0 e^{-\frac{E_a}{RT}} \times \frac{([E]^{0.5}[F]^2)}{(1+K_1(ads)[F]^2+K_3(ads)[E]^{0.5})^2} )</td>
</tr>
<tr>
<td>M2</td>
<td>( r = k_0 e^{-\frac{E_a}{RT}} \times \frac{[K_1K_2[E^{0.5}[F^2]]}{(1+(K_1[E]^{0.5})+(K_2[F^2]))^2} )</td>
</tr>
<tr>
<td>M3</td>
<td>( r = \left( \frac{K_1K_2K_3k_2k_1}{2} \right)^{0.5} \frac{L^2[E]^{0.5}[F]^{0.5}}{(1+(2K_2k_1)} \left( \frac{K_1K_2K_3k_2k_1}{K_1K_3k_2} \right)^{0.5} \left( \frac{[E]^{0.5}[F]^{0.5}}{[F]^{0.5}} \right)^2 )</td>
</tr>
</tbody>
</table>

**A=C_3H_8O_3; B=H_2O; C=O_2; D=CH_4; E=CO_2; F=H_2; Z=CH_4O; S=active site **
3.8 Parameter Estimation

The values of the parameters were estimated using Non-linear Regression Software (NLREG) which is based on Gauss-Newton and Levenberg-Marquardt technique alongside with MATLAB (Gauss Newton). Ibrahim et al. (2006) termed the former methodology as the minimization algorithm due to its ability to determine the sum of squared residuals for a parameter and works further to reduce the parameter value in order to analyze the effect on the sum of squared residuals. The estimates together with their standard errors are given in this chapter.

The tables 3-5 to 3-8 shows the parameter estimation for the kinetic models with NLREG software. Reversible and Irreversible Arrhenius power law models were also tested. An irreversible reaction in the forward direction best describes the overall power law model. This is because; the frequency factor of the forward reaction is far greater than that of the reverse. This indicates that the rate is faster in the forward direction than in the reverse direction. As such, the irreversible power law rate expression can be used to describe the overall kinetics of the ATR system. Power law rate law expression was found for the individual reactions as well as mechanistic models. The results are found from table 3-5 to 3-8.

In addition, parity plots were drawn to analyze the deviation of the predicted rates from the experimental ones. From the analysis, models with percent average absolute deviation (AAD) of more than 20 % were neglected. Afterwards, MATLAB 2017a was used to regress the parameters again to deduce the standard error of each parameter for the successful models. The parity plots of the independent reactions are shown in the figures 3-1 to 3-4:
Table 3-5: Estimate for overall Power Law

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Irreversible</th>
<th>Reversible</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{0f}$ [mol(^{\text{gcat.min}})]</td>
<td>$4.3 \times 10^{10}$</td>
<td>$3.39 \times 10^{5}$</td>
</tr>
<tr>
<td>$E_f$ [(J) mol(^{-1})]</td>
<td>$8.78 \times 10^{4}$</td>
<td>$4.31 \times 10^{4}$</td>
</tr>
<tr>
<td>M</td>
<td>1.04</td>
<td>$-3.48 \times 10^{-5}$</td>
</tr>
<tr>
<td>N</td>
<td>0.54</td>
<td>-0.017</td>
</tr>
<tr>
<td>o</td>
<td>1.78</td>
<td>$9.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>$k_{0r}$ [mol(^{\text{gcat.min}})]</td>
<td>-</td>
<td>$1.38 \times 10^{3}$</td>
</tr>
<tr>
<td>$E_r$ [(J) mol(^{-1})]</td>
<td>-</td>
<td>$4.3 \times 10^{4}$</td>
</tr>
<tr>
<td>Q</td>
<td>-</td>
<td>4.03</td>
</tr>
<tr>
<td>R</td>
<td>-</td>
<td>-4</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>$-8 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Table 3-6: Parameter Estimation for Steam Reforming via NLREG Software

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PLM</th>
<th>ER_3</th>
<th>ER_4</th>
<th>ER_5</th>
<th>ER_7</th>
<th>ER_8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$</td>
<td>8.43 $\times 10^{11}$</td>
<td>1.57 $\times 10^9$</td>
<td>1.33 $\times 10^5$</td>
<td>1.74 $\times 10^8$</td>
<td>3.9 $\times 10^9$</td>
<td>4.16 $\times 10^5$</td>
</tr>
<tr>
<td>$E_a$</td>
<td>8.91 $\times 10^4$</td>
<td>9.23 $\times 10^4$</td>
<td>9.33 $\times 10^4$</td>
<td>9.14 $\times 10^4$</td>
<td>9.23 $\times 10^4$</td>
<td>9.32 $\times 10^4$</td>
</tr>
<tr>
<td>$m$</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$n$</td>
<td>10.37</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_p/K_3$</td>
<td>-</td>
<td>3.47 $\times 10^4$</td>
<td>3.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_B$</td>
<td>-</td>
<td>62.60</td>
<td>0.0168</td>
<td>164.894</td>
<td>155.313</td>
<td>0.00317</td>
</tr>
<tr>
<td>$K_A$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.65 $\times 10^8$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_W$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_Q$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_F$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_1$</td>
<td>-</td>
<td>6.6 $\times 10^4$</td>
<td>1.7 $\times 10^6$</td>
<td>-</td>
<td>1.64 $\times 10^5$</td>
<td>3.07 $\times 10^5$</td>
</tr>
<tr>
<td>$K_c$</td>
<td>-</td>
<td>3.93 $\times 10^7$</td>
<td>2.04 $\times 10^{11}$</td>
<td>3.67 $\times 10^{-5}$</td>
<td>9.76 $\times 10^7$</td>
<td>3.55 $\times 10^{10}$</td>
</tr>
</tbody>
</table>
Table 3-7: Parameter Estimation for Total Oxidation via NLREG software.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PLM</th>
<th>ER_4</th>
<th>ER_5</th>
<th>LHHW_2a</th>
<th>LHHW_6</th>
<th>LHHW_7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0 \left( \frac{g_{cat}}{min} \right)$</td>
<td>2.95 x 10^{10}</td>
<td>2.22 x 10^4</td>
<td>5.3 x 10^3</td>
<td>3.9 x 10^3</td>
<td>2.96 x 10^5</td>
<td>5.17 x 10^7</td>
</tr>
<tr>
<td>$E_a \left( \frac{J}{mol} \right)$</td>
<td>8.88 x 10^4</td>
<td>5 x 10^4</td>
<td>4.78 x 10^4</td>
<td>4.83 x 10^4</td>
<td>7.26 x 10^4</td>
<td>6.31 x 10^4</td>
</tr>
<tr>
<td>m</td>
<td>-0.44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n</td>
<td>3.47</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_p$</td>
<td>-</td>
<td>8.99 x 10^{-4}</td>
<td>4.41 x 10^{-5}</td>
<td>4.25 x 10^{-5}</td>
<td>1.08 x 10^{-10}</td>
<td>-</td>
</tr>
<tr>
<td>$K_B$</td>
<td>-</td>
<td>3.63 x 10^3</td>
<td>7.06 x 10^{-4}</td>
<td>1.38 x 10^{-3}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_A$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.45 x 10^4</td>
<td>538.03</td>
<td>-</td>
</tr>
<tr>
<td>$K_W$</td>
<td>-</td>
<td>2.42 x 10^4</td>
<td>1.07 x 10^5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_c$</td>
<td>-</td>
<td>4.19 x 10^{-4}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_1$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.07 x 10^5</td>
<td>0.46</td>
<td>0.52</td>
</tr>
<tr>
<td>$K_2$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
</tr>
<tr>
<td>$K_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.91 x 10^{-4}</td>
<td>0.0166</td>
<td>-</td>
</tr>
<tr>
<td>$K_5$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.62 x 10^3</td>
<td>-</td>
</tr>
<tr>
<td>$K_3$</td>
<td>-</td>
<td>4.38 x 10^5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 3-8: Parameter Estimation for CO2 Methanation via NLREG Software.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PLM</th>
<th>ER_1</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0 \left( \frac{g_{\text{cat}}}{\min} \right)$</td>
<td>1.51 $\times 10^3$</td>
<td>8.55 $\times 10^6$</td>
<td>8.285E+011</td>
<td>4.48 $\times 10^3$</td>
<td>-</td>
</tr>
<tr>
<td>$E_a \left( \frac{l}{mol} \right)$</td>
<td>8.86 $\times 10^4$</td>
<td>8.06 $\times 10^4$</td>
<td>9.35 $\times 10^4$</td>
<td>4.14 $\times 10^2$</td>
<td>-</td>
</tr>
<tr>
<td>M</td>
<td>-2.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N</td>
<td>-0.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_p$</td>
<td>27.94</td>
<td>2.54 $\times 10^{-4}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_{10}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.33 $\times 10^3$</td>
</tr>
<tr>
<td>H1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>25.83</td>
</tr>
<tr>
<td>H2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>94.46</td>
</tr>
<tr>
<td>$K_2$</td>
<td>-</td>
<td>-</td>
<td>6.94 $\times 10^8$</td>
<td>3.39 $\times 10^2$</td>
<td>1.7 $\times 10^4$</td>
</tr>
<tr>
<td>$K_1$</td>
<td>-</td>
<td>1.29 $\times 10^3$</td>
<td>5.96 $\times 10^2$</td>
<td>7.44 $\times 10^{-3}$</td>
<td>6.07 $\times 10^3$</td>
</tr>
<tr>
<td>$K_3$</td>
<td>-</td>
<td>3.15 $\times 10^4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>k11</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.32 $\times 10^3$</td>
</tr>
<tr>
<td>k4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.33</td>
</tr>
<tr>
<td>L</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.73 $\times 10^3$</td>
</tr>
</tbody>
</table>
Figure 3-1: Parity plot of Experimental against Predicted rate

Figure 3-2: Parity plot for Steam reforming.
Figure 3-3: Parity plot for Total Oxidation

Figure 3-4: Parity plot for CO2 Methanation.
The parameters of the successful models with their corresponding standard error were obtained using an in-built solver (fit nonlinear regression model (fitnlm)) in MATLAB 2017a. The results for the various models between that obtained by NLREG and MATLAB were quite different. This could be because of the difference in the solution algorithm used by these softwares. NLREG uses both Gauss-Newton and Levenberg-Marquardt whereas fitnlm in MATLAB uses only Levenberg-Marquardt. A summary of the parameters is as shown in the tables 3-10 to 3-12. A parity plot for experimental rate against predicted rate for the total oxidation reaction using MATLAB was done since the NLREG model predicted higher AAD.
Table 3-9: Parameter estimation for steam reforming using MATLAB 2017

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PLM</th>
<th>ER 5</th>
<th>ER 3</th>
<th>ER 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0$ $[\text{mol/}g\cat\text{.min}]$</td>
<td>$4.13 \times 10^{12}$ $\pm 3.69 \times 10^{5}$</td>
<td>$5.32 \times 10^{7}$ $\pm 4.1 \times 10^{6}$</td>
<td>$9.014 \times 10^{-1}$ $\pm 3.5 \times 10^{-2}$</td>
<td>$1.17 \times 10^{5}$ $\pm 9.9 \times 10^{3}$</td>
</tr>
<tr>
<td>$E_a$ $[\text{J/mol}]$</td>
<td>$9.08 \times 10^{4}$ $\pm 2.2 \times 10^{3}$</td>
<td>$9.11 \times 10^{4}$ $\pm 4.8 \times 10^{3}$</td>
<td>$9.1208 \times 10^{4}$ $\pm 4.26 \times 10^{3}$</td>
<td>$9.32 \times 10^{4}$ $\pm 1.57 \times 10^{2}$</td>
</tr>
<tr>
<td>M</td>
<td>$2.29 \pm 0.07$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>$12.8 \pm 0.97$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_p = K_3$</td>
<td>-</td>
<td>-</td>
<td>$1.17 \times 10^{9}$ $\pm 5.85 \times 10^{6}$</td>
<td>$1.13 \times 10^{9}$ $\pm 4.65 \times 10^{6}$</td>
</tr>
<tr>
<td>$K_B$</td>
<td>-</td>
<td>$6.85 \times 10^{7}$ $\pm 1.13 \times 10^{6}$</td>
<td>$3.85 \times 10^{-4}$ $\pm 1.99 \times 10^{-10}$</td>
<td>$1.35 \times 10^{6}$ $\pm 4.5 \times 10^{4}$</td>
</tr>
<tr>
<td>$K_A$</td>
<td>-</td>
<td>$4.2 \times 10^{-9}$ $\pm 1.6 \times 10^{-13}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parameter</td>
<td>PLM</td>
<td>LHHW 2</td>
<td>LHHW 7</td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td>----------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td>(K_1)</td>
<td>-</td>
<td>-</td>
<td>1.79 (\times 10^{-7}) ± 1.6 (\times 10^{-8})</td>
<td>1.56 (\times 10^{-2}) ± 1 (\times 10^{-3})</td>
</tr>
<tr>
<td>(K_c)</td>
<td>-</td>
<td>2.73 (\times 10^{-6}) ± 2.37 (\times 10^{-7})</td>
<td>4.67 (\times 10^{-2}) ± 1.11 (\times 10^{-3})</td>
<td>2.74 (\times 10^{11}) ± 2 (\times 10^{6})</td>
</tr>
</tbody>
</table>

Table 3-10: Parameter Estimation for Total Oxidation using MATLAB 2017
<table>
<thead>
<tr>
<th>Parameter</th>
<th>PLM</th>
<th>ER_1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_0 \left( \frac{gcat}{min} \right)$</td>
<td>$1.506 \times 10^3 \pm 6.20 \times 10^1$</td>
<td>$8.84 \times 10^6 \pm 7.2 \times 10^{-23}$</td>
</tr>
<tr>
<td>$E_a \left( \frac{J}{mol} \right)$</td>
<td>$8.9 \times 10^4 \pm 1.04 \times 10^3$</td>
<td>$8.12 \times 10^4 \pm 5.6 \times 10^3$</td>
</tr>
<tr>
<td>$M$</td>
<td>$-2.089 \pm 6 \times 10^{-2}$</td>
<td>-</td>
</tr>
<tr>
<td>$N$</td>
<td>$-0.2 \pm 4.87 \times 10^{-3}$</td>
<td>-</td>
</tr>
<tr>
<td>$K_p$</td>
<td>$2.79 \times 10^1 \pm 1.12$</td>
<td>$6.79 \times 10^{-5} \pm 3.95 \times 10^{-6}$</td>
</tr>
<tr>
<td>$K_1$</td>
<td>-</td>
<td>$7.435 \times 10^2 \pm 2.76 \times 10^1$</td>
</tr>
<tr>
<td>$K_3$</td>
<td>-</td>
<td>$7.6 \times 10^4 \pm 8.3 \times 10^2$</td>
</tr>
</tbody>
</table>

Table 3-11: Parameter Estimation for CO₂ Methanation using MATLAB 2017
Figure 3-5: Parity plot for TOR using MATLAB 2017
Chapter 4 : Reactor Model Development

4.1 Synopsis

Projections made by International Energy Outlook in 2018 stipulated that the energy consumption of non-OECD (Organization for Economic Cooperation and Development) countries has surpassed that of OECD ones in 2007 and by 2040, an estimation of 493 quadrillion Btu is expected to be reached. Also, the energy consumption in the non-OECD (Organization for Economic Cooperation and Development) countries has exceeded the OECD consumption in 2007 and is projected to reach nearly two-thirds of the 739 quadrillion Btu global energy consumption in 2040”. This implies that, the non-OECD countries are rapidly consuming energy as much as the OECD ones and thus, every country is contributing to greenhouse emissions irrespective of the classification. This comparatively conveys the amount of emissions released into the environment as per the increase in energy consumption. Energy consumption from burning fossil fuels emits some greenhouse gases like carbon dioxide, methane and nitrous oxide which causes global warming. The most common cause of this calamity is the use of fossil fuels. Therefore, energy sources which will safeguard the environment will provide prudent way to solve this problem. Using renewable energy sources, which will serve the same purpose as fossil fuels, is a step in the right direction to reduce this global problem. One of the most significant renewable energy sources is biomass (Sadooghi and Rauch, 2014).

Biodiesel, a source of biomass is considered in this work which serves as a surrogate for fuel and reduces the dependence on fossil fuel. Biodiesel is biodegradable and non-toxic. It can be produced via transesterification reaction of oils (vegetable and animal fat oil) in the presence of a catalyst. In fact, 3 moles of fatty acid methyl esters (FAME) produces 1
mole of glycerol. There are little to no uses for this crude glycerol produced thus, making the crude glycerol an unwanted product. No available technology is commercialized enough to match up the high amounts of crude glycerol produced, and refinery of the crude glycerol is cost intensive as well. The commonest use of crude glycerol is to purify prior to use in food and pharmaceutical industries (small amount) or to water treatment plants for digestion (Adhikari et al., 2007, Ma and Hanna, 1999, Tapanes et al., 2008, Nopharatana et al., 2006).

Hydrogen as a source of energy has gained great interest amongst scientist today due to great benefits as against that from non-renewable sources. The most popular application of hydrogen production is in fuel cells. There are vast processes of producing hydrogen which includes electrolysis and thermal splitting, pyrolysis, biological and photobiological and reforming techniques like Steam reforming (most commonly used and industrialized), aqueous phase reforming, partial reforming, supercritical water reforming, autothermal reforming and others (Dhamrat and Ellzey, 2006). The production of hydrogen via these processes is carried out in a reactor where the processes are categorized as endothermic or exothermic.

4.2 Model Solution

The two (2) main methods for solving differential equations are namely analytical and numerical solutions. Analytical solution involves finding the exact solution, which provides values of the dependent variables at any position and time. The conservative equations are nonlinear in nature and hence numerical solution provides a feasible solution option (Esch et al., 2005; Rout and Jakobsen, 2015). Before choosing a numerical method,
the degree of convergence and computational flexibility of the numerical method is of primary essence. Numerical techniques available include Finite difference, Finite Element, Spectral Methods (sub category of Weighted Residuals), Boundary Element and other methods are already in literature (Rout and Jakobsen, 2015; Kreyszig, 2005; Esch et al., 2005). According to Rout and Jakobsen, 2015; Smith, 1985; Schiesser, 1991, the most common numerical methods used for engineering purposes are Finite difference, Finite Volume and Finite Element.

Bischoff and Froment (1979) classified fixed bed reactors based on the number of phases present in the reactor and hence, homogenous and heterogeneous models were established. In this work, 1-dimensional pseudo-homogenous and heterogeneous models were developed in MATLAB 2017a. Based on the design equations, codes were written to solve for temperature and species concentration. The schematic diagram for the reactor is shown in figure 4-1.

4.1 Governing Equations

4.1.1 One (1) D Pseudo-homogenous model

This model is used when the equilibration between solid and fluid occurs fast enough compared with the time scale of the process. A one (1) -dimensional pseudo homogenous model is designed to study the autothermal reforming (ATR) of crude glycerol in a fixed bed reactor. The behavior of the process was studied as it was made to solve through dynamic conditions until steady state conditions were reached in the reactor. The major assumptions considered in this model are as follows:
• Both phases (gas and solid) are assumed as a single phase and a set of equations is written to describe the transport phenomena.

• Ideal gas behavior was assumed.

• The gas and solid phase are assumed to exist as one phase.

• Temperature and mass fraction considered only in the axial direction.

• Constant bed porosity

• Seven species (N\textsubscript{2}, CH\textsubscript{4}, O\textsubscript{2}, C\textsubscript{3}H\textsubscript{8}O\textsubscript{3}, CO\textsubscript{2}, H\textsubscript{2}, H\textsubscript{2}O) are involved in the model.

• Constant pellet size throughout the reactor.

• Incompressible fluid

• Constant effectiveness factor due to small pellet size which resulted in negligible mass transfer limitations (Pantoleontos et al., 2012; Hou et al., 2001).

4.1.1.1 Design Equations for pseudo-homogenous model

The design equation used in this work comprises of a set of PDEs. The main reference used for this model was based on the equations found in Rout and Jakobsen (2015). With the assumption of a single-phase model, one set of equation is written to describe the mass/mole fraction, pressure and temperature within the fixed bed reactor. The reaction source term which contains the reaction term is derived from the kinetics discussed in the previous section. The mechanistic model was not used due to the complex nature of the rate law expression and thus, power law model was used for simplicity.

The design equations are as shown below

• The general form of the continuity equation which is obtained by adding up the species terms \( \sum w_j = 1 \) and \( \sum J_j = 1 \) in the species equation.

Where \( w_j \) is the mass fraction of species \( j \) and \( J_j \) is the diffusion flux of species \( j \)
\[ \varepsilon_p \frac{d \rho_g}{d t} + \frac{\partial}{\partial z} u_z \rho_g = 0 \]  

(4.1)

- The general energy equation which is constructed in terms of temperature is given as:

\[
\left[ (1 - \varepsilon_p) C'_p \rho_p + \varepsilon_p \rho_g C'_{p,g} \right] \frac{\partial T}{\partial t} + \rho_g C_{p,g} u_z \frac{\partial T}{\partial z} = -\frac{\partial}{\partial z} (Q_Z) + \frac{4u}{d_t} (T_W - T') + S'
\]

(4.2)

\[
Q_Z = -k \frac{\partial T}{\partial z}
\]

(4.3)

The source term is \( S' = (1 - \varepsilon_p) \rho_p \sum_k (\Delta H_{rxn,k}) (\eta_k R_k) \)  

(4.4)

The first term represents the rate of accumulation of heat; the second is the net advection flux; the third is the heat conducted through the reactor; the fourth is the heat convection term which is negligible due to the insulation of the reactor walls and the last term is the reaction source term.

- The general form of the species equation which is solved for each of the reacting species is given as:

\[
\frac{\partial}{\partial t} \left( \varepsilon_p \rho_g w_j \right) + \frac{\partial}{\partial z} \left( \rho_g u_z w_j \right) - \frac{\partial}{\partial z} \left( \varepsilon_p \rho_g D_{L,j} \frac{\partial w_j}{\partial z} \right) = S_j
\]

(4.5)

\[
S_j = (1 - \varepsilon_p) \rho_p M_j \sum_k (v_{jk}) (\eta_k R_k)
\]

(4.5 a)

The first term is the rate of accumulation of species followed by the advection term then the diffusion flux of the species, \( j \) and finally, the reaction source term.

- The pressure drop given by Ergun’s equation found in Routs and Jakobsen (2015)

\[
\frac{\partial p}{\partial z} = -(k_{di} u_z + k_{vi} u_z^2)
\]

(4.6)

where \( k_{di} \) and \( k_{vi} \) represent the viscous and kinetic pressure drop in the reactor with the corresponding units of Pas/m² and Pas²/m³ respectively.
\[ k_{dl} = \frac{150 \mu (1-\varepsilon_p)^2}{d_p^2 \varepsilon_p^3} \quad (4.7) \]
\[ k_{vl} = \frac{1.75 \rho_g (1-\varepsilon_p)}{d_p \varepsilon_p^3} \quad (4.8) \]

- Ideal gas Law (calculation of Mixture density in kg/m³)
\[ \rho_g = \frac{P}{RT} \quad (4.9) \]

- Bed porosity
\[ \varepsilon_p = 0.38 + 0.073 \times \left( 1 + \left( \frac{D}{d_p} \right)^2 \right) \quad (4.10) \]
Figure 4-1: Schematic diagram of Fixed Bed Reactor
4.1.1.2 Boundary and Initial Conditions

The boundary and initial conditions are very paramount since they significantly influences the solution. The main boundary conditions used in this model were the Neuman and Dirichlet boundary conditions. The neuman boundary condition was used on the exit based on the assumption that the flow was advected out of the reactor with the velocity. The pressure reported by Ghani et al., 2017 was atmospheric throughout the reactor. For the sake of simplicity, the assumption that the reported pressure was taken as the outlet pressure and an inlet pressure slightly higher than the outlet was assumed. Based on this assumption, two Dirichlet boundary conditions were used for the pressure term whereas Dirichlet and Neuman boundary conditions were used for the species and temperature equation. A summary of the initial and boundary conditions for 1-d pseudo homogenous model is shown in table 4-1.

4.1.1.3 Algorithm for pseudo-homogenous Numerical Solution

The design equations for this model are discretized using a cell-centered finite difference scheme with uniform cell sizes. Pseudo transient approach was used where the solution was monitored through unsteady till steady state. Accumulation and advection terms were discretized using forward difference and upwinding differencing scheme respectively whereas the conduction and diffusion terms were discretized using the central difference approach. The pressure-velocity coupling was solved at time t=0 by initially solving the Ergun’s equation considering the pressure boundary conditions. At time t greater than zero (t>0),

- The design equations are solved in a time loop. The general mass balance and energy equation is solved simultaneously for both pressure and temperature.
• The velocity is recalculated by Ergun’s equation
• The species equation is solved to obtain the mass fractions of the individual species
• Other supporting equations like specific heat capacity, heat of reaction, reaction rate, viscosity, average molecular weight and reaction source terms are solved and updated at each time loop.
• The algorithm is solved with time where the variables are stored, and the graphs plotted to observe the growing trends.

A schematic diagram of the solution matrix is shown in figure 4-2

4.1.2 One (1) D Heterogeneous Model

This model accounts for the concentration and temperature gradient between the catalyst pellet and bulk gas. The process was modelled the same way as the pseudo homogenous. The only exception is the additional set of equations written for the solid phase. The major assumptions considered in this model were:

• The solid and gaseous phase are taken as two (2) phases and different set of equations are written to describe each phase. This phase considers the concentration gradient between the fluid and solid phases as well.
• Ideal gas law.
• Negligible pressure drop and constant velocity.
• Temperature and mass fraction considered only in the axial direction.
• Constant bed porosity.
• Seven species (N₂, CH₄, O₂, C₃H₈O₃, CO₂, H₂, H₂O) were involved in the model.
• Constant pellet size throughout the reactor.
- Incompressible fluid.
- Specific heat capacity, thermal conductivity and viscosity a function of local temperature and composition in the reactor.

Figure 4-2: Schematic diagram for 1-d pseudo-homogenous solution approach.
4.1.2.1 Design Equation

The design equations for this model were obtained from Rout and Jakobsen (2015) and Croon and Halabi (2008). The governing equations used were:

**Fluid phase**

Species:

\[ \varepsilon_p \frac{\partial \rho_g w_j}{\partial t} + \frac{\partial u_z \rho_g w_j}{\partial z} + a_v k_{g,j} \rho_g (w_j - w_j^s) = \varepsilon_p \rho_g D_{L,j} \frac{\partial^2 w_j}{\partial z^2} \]  

Energy:

\[ \varepsilon_p \rho_g C_p g \frac{\partial T}{\partial t} + u_z \rho_g C_p g \frac{\partial T}{\partial z} = h a_v (T_s - T) + \lambda \frac{\partial^2 T}{\partial z^2} \]  

General continuity:

\[ \varepsilon_p \frac{\partial \rho_g}{\partial t} + \frac{\partial u_z \rho_g}{\partial z} = \sum_k a_v k_{g,j} \rho_g (w_j - w_j^s) \]  

**Solid Phase**

The pellet phase equations are solved explicitly for the values. Due to the small particle size of the catalyst pellet, an assumption of negligible rate of accumulation of concentration in the pellet was made (Rout and Jakobsen, 2015; Croon and Halabi, 2008).

Species:

\[ a_v k_{g,j} \rho_g (w_j - w_j^s) = (1 - \varepsilon_p) \rho_p M_j \sum_k (v_{j,k})(\eta_k R_k) \]  

Energy:

\[ (1 - \varepsilon_p) \rho_p C_p \rho \frac{\partial T_s}{\partial t} + h a_v (T_s - T) = \rho_p \frac{1 - \varepsilon_p}{\sum_k (\Delta H_{rxn,k}) (\eta_k R_k)} \]  

91
### Table 4-1: Initial and Boundary Condition for PH and HET Model (MATLAB)

<table>
<thead>
<tr>
<th>Initial Conditions (t=0)</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P</strong>=<strong>P</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
<td>At z=0 ; <strong>P</strong>&lt;sub&gt;in&lt;/sub&gt;=<strong>P</strong>&lt;sub&gt;w&lt;/sub&gt;</td>
</tr>
<tr>
<td><strong>T</strong>= <strong>T</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
<td><strong>T</strong>= <strong>T</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
</tr>
<tr>
<td><strong>W</strong>&lt;sub&gt;j&lt;/sub&gt;=<strong>W</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
<td><strong>W</strong>&lt;sub&gt;j&lt;/sub&gt;=<strong>W</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

Initial and Boundary Condition for HET Model (MATLAB)

<table>
<thead>
<tr>
<th>Initial Conditions (t=0)</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P</strong>=<strong>P</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
<td>At z=0 ; <strong>P</strong>&lt;sub&gt;in&lt;/sub&gt;=<strong>P</strong>&lt;sub&gt;w&lt;/sub&gt;</td>
</tr>
<tr>
<td><strong>T</strong>= <strong>T</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
<td><strong>T</strong>= <strong>T</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
</tr>
<tr>
<td><strong>T</strong>&lt;sub&gt;s&lt;/sub&gt;= <strong>T</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
<td><strong>W</strong>&lt;sub&gt;j&lt;/sub&gt;=<strong>W</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
</tr>
<tr>
<td><strong>W</strong>&lt;sub&gt;j&lt;/sub&gt;=<strong>W</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
<td><strong>W</strong>&lt;sub&gt;j&lt;/sub&gt;&lt;sub&gt;s&lt;/sub&gt;=<strong>W</strong>&lt;sub&gt;in&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

At z=L; **P**<sub>out</sub>=**P**<sub>E</sub>

\[
\frac{dT}{dZ} = 0 \\
\frac{dW_j}{dZ} = 0
\]
4.1.2.2 Algorithm for Heterogeneous Numerical Solution

The algorithm for the 1-D HET model is identical to the 1-d PH model where the pressure and temperature for the bulk gas was solved simultaneously. The species mass fraction is solved right afterwards. The velocity is updated as well as the axial dispersion of the species. Based on the species mass fraction in the bulk gas, the solid phase energy and species equations are solved as well. The Reynolds number, specific heat capacity, Nusselt number, Schmidt’s and Sherwood number, Mass transfer coefficient, heat of reaction, partial pressure, rate of reaction and reaction source terms are updated respectively. These new values return to the loop where they are solved.
Solve P and T simultaneously

Solve Ergun equation for velocity update

Solve species equation for the mass fraction for fluid phase

Convert Mass fraction ($w_j$) to mole fraction ($y_A$)

Solve Temperature equation for the solid phase

Solve species equation for the mass fraction for fluid phase

Update Molar mass, Specific heat, Heat of Reaction

Update for partial pressures using ($P_A = y_A * P_T$)

Solve and update reaction term

Solve and update temperature source term

Solve and update species source term

$t < nt * dt$

Figure 4-3: Solution Approach to HET model in MATLAB
4.2 Modelling with COMSOL Multiphysics

COMSOL Multiphysics is a graphical user interface which is designed to implement finite element numerical methods to solve the partial differential equations (PDEs) and differential algebraic equations (DAEs). This software is widely used to simulate and model science and engineering problems facing the world today. Upon opening the COMSOL Multiphysics software, the model wizard allows a user to first choose a spatial dimension which ranges from between 0-3 dimensions. Afterwards, the physics that best describes the problem is chosen from the given list embedded in the program. These modules (physics) are categories of relevant equations where a user can enter the input parameters for the programme to solve for outputs. In addition, the governing equations listed in COMSOL can be modified based on the requirements of the user. Some modules available are AC/DC, Chemical species transport, Δu Mathematics, heat transfer in fluids, heat transfer in porous media etc and the major types of study the user desires are classified into stationary plug flow, time dependent and custom studies. Several works have been done using COMSOL Multiphysics. The commonest module for reactor or storage tank design is via pseudo-homogenous approach by Afagbor et al., 2017; Schlereth and Hinrisch,2014; Muthukumar et al,2012; William (2017); Freni et al.,2009. The version 5.2 of COMSOL Multiphysics was used in this thesis.

4.2.1 2 Two (2) D Pseudo-Homogenous Model

A tubular reactor as shown in figure 4-1 is modelled in COMSOL Multiphysics considering heat transfer and transport of species in the radial and axial directions. A gaseous crude glycerol/water mixture with inlet temperature, T0 and initial mole fraction of reactants C₃H₈O₃=0.0948, O₂=0.0587 and H₂O=0.61 were introduced into the reactor.
The transport equations considered in this model are mass, heat and momentum which are a set of partial differential equations. Additionally, the reactions and compressibility of the gaseous phase were all accounted (Palma et al, (2016); Diglio et al., (2016)). The numerical solution was done by finite element method. The main assumptions utilized in this model were:

- Gaseous species present in the mixture were assumed to be ideal gases.
- The fluid and solid phase are taken as a single phase and one (1) set of equation is written to describe this phase.
- Compressible fluid (that is the variation of density within the reactor).
- The design equations were evaluated in cylindrical co-ordinates for the 2-Dimensional model and the reactor was operated at atmospheric pressure (Afagbor et al., 2017).
- This model is a time independent model that is, it represents a stationary study of the reactor and the reactor was assumed to be axisymmetric (Chein et al., 2013).
- Constant physical properties like molecular diffusivity, viscosity and thermal conductivity (He, 2003).

4.2.2 Design Equations for 2D pseudo-homogenous model

According to Schlereth and Hinrichsen (2014), an assumption that porosity was unconstrained by the radial position in the reactor was used. Under reacting flow in porous media, the no slip condition at the walls was catered for. The kinetic term described by the power law model was incorporated as well. The design equations were developed based on modifications made by Schlereth and Hinrichsen (2014), Afagbor et al., (2017) and Diglio et al. (2016).
Mass Balance:

\[ D_{z,r,j} \left( \frac{\partial^2 C_j}{\partial r^2} + \frac{1}{r} \frac{\partial C_j}{\partial r} \right) + D_z \frac{\partial^2 C_j}{\partial z^2} - u_z \frac{\partial C_j}{\partial z} = (1-e_p) \rho_p \sum_k v_{jk} (-R_k) M_{jk} \]  

(4.16)

Energy Balance:

\[ \lambda_{er} \left( \frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \lambda_{ez} \frac{\partial^2 T}{\partial z^2} - C_{pg} \rho_g u_z \frac{\partial T}{\partial z} = (1-e_p) \rho_p \sum_k (-\Delta H_{rxn,k}) M_{jk} \]  

(4.17)

### 4.2.3 Two (2) D Heterogeneous Model (Pseudo Heterogenous)

According to Froment, 1972, heterogeneous model explicitly accounts for both the solid and fluid phases. The complexity of the models is dependent on the category of the model under discussion. The modules used were heat transfer and transport of diluted species. The set of partial differential equations (PDEs) are solved numerically using finite element method in COMSOL Multiphysics. The model similar to the packed bed reactor in application libraries was followed and modified to meet the requirements of this work. The bulk gas initial and boundary conditions is the same as pseudo homogenous. The main assumptions utilized in this model are:

- Ideal gas.
- Incompressible fluid
- Design equations evaluated in cylindrical co-ordinates for the 2-Dimensional model and the reactor is operated at atmospheric pressure (Afagbor et al., 2017).
- Constant physical properties like molecular diffusivity, viscosity and thermal conductivity (He, 2003; Akpan et al., (2007)). Also, constant velocity, constant bed void fraction and uniform catalyst throughout the reactor.
Table 4-2: Initial and Boundary conditions for 2D pseudo homogenous and heterogeneous model

<table>
<thead>
<tr>
<th>Initial and Boundary conditions for 2D Pseudo Homogenous model.</th>
<th>Initial Conditions ((z=0, 0 \leq r \leq D))</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P=P_{in}) (C_{j,(r,0)} = C_{j,in}) (T_{(r0)} = T_{in})</td>
<td>At (r=0, 0 \leq z \leq L); (\frac{\partial C_j}{\partial r(0,z)} = 0) (\frac{\partial T}{\partial r(0,z)} = 0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>At (r=\frac{D}{2}, 0 \leq z \leq L); (\Lambda_{ez} \frac{\partial T}{\partial r(DL)} = -U_A(T - T_0)) (\frac{\partial C_j}{\partial r(D,0)} = 0)</td>
<td></td>
</tr>
</tbody>
</table>

Initial and Boundary conditions for 2D Heterogeneous model.

Bulk gas B.C same as that of 2D pseudo homogenous

<table>
<thead>
<tr>
<th>Initial Conditions ((r=r_p \text{ (surface)}))</th>
<th>Boundary Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_{x_j} \frac{dC_{j,s}}{dr} = k_{gj} a_v \ (C-C_{j,p}))</td>
<td></td>
</tr>
</tbody>
</table>
4.2.4 Conservation Equations for 2D Heterogeneous Model

Properties (like thermal conductivity, densities and specific heat capacity) of the solid and gas phase are written as parameters in this software. The design equations considered in this model were based on the modifications given by Froment, 1972; Palma et al. (2016) and Williams, 2017. Since this model is a stationary study, the rate of accumulation of concentration and Temperature is neglected from the equation. The design equations are as shown:

Mass Balance for bulk gas:

\[
D_{zr,j}\left(\frac{\partial^2 C_j}{\partial r^2} + \frac{1}{r}\frac{\partial C_j}{\partial r}\right) + D_{z,j}\frac{\partial^2 C_j}{\partial z^2} - u_z \frac{\partial C_j}{\partial z} = k_{gi} a_v (C_j - C_{js})
\]  

(4.18)

The first and second terms are the diffusion flux in the radial and axial directions respectively which accounts for the mass transfer in the reactor. The third term is the advection flux in the reactor and the term on the right-hand side accounts for the mass transfer between the phases.

Energy Balance for bulk gas:

\[
\lambda_{zr}\left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + \lambda_{z,j}\frac{\partial^2 T}{\partial z^2} - u_z \rho_g c_{pg} \frac{\partial T}{\partial z} = h a_v (T - T_p)
\]  

(4.19)

The first two (2) terms account for the heat conduction in the radial and axial direction whereas the third term is the heat advection flux in the reactor and finally, the term on the right-hand side is the convective heat transfer between the two (2) phases (ie bulk gas and solid phases respectively)

Mass Balance for solid phase:
\[ \frac{1}{r_p} D_{z,j} \frac{\partial}{\partial r} \left( r_p \frac{\partial C_{j,s}}{\partial r} \right) = (1 - e_p) \rho_p \sum_k \nu_{jk} (-\eta_k R_k) \]  \hspace{1cm} (4.20)

Energy Balance
\[ \frac{1}{r_p} \frac{\lambda}{\lambda_{zr,s}} \frac{\partial}{\partial r} \left( r_p \frac{\partial T_p}{\partial r} \right) = (1 - e_p) \rho_p \sum_k \left(-\Delta H_{r,\text{rxn},k}\right) (\eta_k R_k) \]  \hspace{1cm} (4.21)

(Williams, 2017; He ,2003; Akpan,2008)

The parameters for the governing equations for both pseudo-homogenous and heterogeneous models are defined as follows: \(C_j\) and \(C_{j,s}\) are concentration of species \(j\) in the bulk gas and the concentration of the species, \(j\) in the solid phase respectively with its units as mol/m\(^3\); \(T\) and \(T_p\) are the temperatures of the bulk gas and solid phase respectively in K; \(e_p\) is the porosity of the catalyst pellet; \(k_{gi}\) is the mass transfer coefficient between the two (2) phases in m/s; \(h\) is the heat transfer coefficient between the gas and solid phase, W/m\(^2\)K; \(D_{z,r,j}\) and \(D_{z,j}\) are the effective radial and axial diffusivity of the mixture respectively with unit as m\(^2\)/s; \(\lambda_{zr}\) and \(\lambda_z\) are the effective radial and axial conductivity of the gas mixture respectively, whereas, \(\lambda_{zr,s}\) is the thermal conductivity of the solid phase with unit as W/mK; \(C_{pg}\) is the specific heat capacity of the bulk gas in J/kgK; \(a_v\) is the surface area to volume ratio of the pellet in m\(^2\)/m\(^3\); \(\rho_g\) and \(\rho_p\) is the gas density and catalyst density respectively in kg/m\(^3\); \(u_z\) is the velocity in the axial direction in m/s; \(v_j\) is the stoichiometric coefficient of component \(j\); \(R_k\) is the rate of reaction, mol/m\(^3\)/s; \(\Delta H_{r,\text{rxn}}\) is the heat of reaction of the mixture in J/mol; the radial and axial spatial coordinates are given as \(z\) and \(r\) in m.

The above illustrates the general presentation of a 2D equations for a fixed bed reactor model. COMSOL Multiphysics has its own presentation of these equations which are
already in built in the program. The equations as stated in COMSOL Multiphysics are as shown below. For a steady state model, \( \alpha, e_a, \gamma \) and \( a \) are equal to zero. Hence, the transport of diluted species and heat transfer is for equation 4.22 is reduced to equation 4.22 a, 4.22 b and 4.22 c. For the sub equations, \( \nabla u \) is replaced by \( \nabla T \); \( \beta \) into \( \rho C_p u \) and \( c \) into \( k \) respectively. These coefficients can be defined as \( Q \), the heat source (W/m\(^3\)); \( \nabla \) is the gradient function, and the term \( f \) is the reaction rate expression (mol/m\(^3\)-s)

\[
e_a \frac{\partial^2 u}{\partial t^2} + e_a \frac{\partial u}{\partial t} - \nabla \cdot (c \nabla u + \alpha u - \gamma) + \beta \cdot \nabla u + au = f \quad (4.22)
\]

\[
- \nabla \cdot (c \nabla u) + \beta \cdot \nabla u = f \quad (4.22 \text{ a})
\]

\[
u \cdot \nabla c = \nabla \cdot (D \nabla c) + R \quad (4.22 \text{ b})
\]

\[
\rho C_p u \cdot \nabla T = \nabla \cdot (k \nabla T) + Q \quad (4.22 \text{ c})
\]
Input parameters from experiments
➢ Inlet temperature
➢ Pressure
➢ Mole fraction of reactants

Calculation of thermophysical properties
Density, thermal conductivity, specific heat capacity, molecular weight

COMSOL Multiphysics Blank Wizard

Dimension specification, Physics (module) type and study selection

Parameters (Boundary condition)
➢ Transport of diluted Species
➢ Heat transfer in fluids/ porous

Variables (Rate law expression, conversion and others, general extrusion)

Study (Stationary)

Results

Post processing of results

Figure 4-4: General COMSOL Multiphysics configuration
4.3 Auxiliary Equations

Table 4-3: Supplementary Equations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat of reaction</td>
<td>$H_{rxn} = H_0 + \int_{T_1}^{T_2} C_p dT$</td>
<td>Fogler, 2011</td>
</tr>
<tr>
<td>Specific Heat Capacity</td>
<td>$C_{pi} = A + BT + CT^2 + DT^3 + ET^4$</td>
<td>Lira and Elliott, 2012</td>
</tr>
<tr>
<td></td>
<td>$C_{pg} = y_i C_{pi}$</td>
<td></td>
</tr>
<tr>
<td>Mixture Density</td>
<td>$\rho_g = \frac{P M_{avg}}{RT}$</td>
<td>Rout and Jakobsen, 2015</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>$D_{AB} = 10^{-3} T^{1.75} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{0.5}$</td>
<td>Incropera et al, 2007</td>
</tr>
<tr>
<td></td>
<td>$P \left[ (\Sigma V_A)^{1/3} + (\Sigma V_B)^{1/3} \right]^{2}$</td>
<td>Rout and Jakobsen, 2015</td>
</tr>
<tr>
<td></td>
<td>$D_{im} = 1 - y_i \frac{\Sigma_{j=1}^{k} \frac{N_{i,j}}{N_i}}{\Sigma_j} \frac{y_j - y_i}{D_{AB,i}}$</td>
<td>Williams (2017)</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>$N_{Re} = \frac{\rho_g u_d d_p}{\mu}$</td>
<td>Perry’s (2008), Croon and Halabi, 2008</td>
</tr>
<tr>
<td>Schmidt’s number</td>
<td>$N_{Sc} = \frac{\mu}{\rho_g D_m}$</td>
<td>Perry’s (2008), Croon and Halabi, 2008</td>
</tr>
<tr>
<td>Prandtl Number</td>
<td>$N_{Pr} = \frac{C_p g \mu}{k}$</td>
<td>Perry’s (2008)</td>
</tr>
<tr>
<td>Sherwood number</td>
<td>$N_{Sh} = \frac{K_g L}{D}$</td>
<td>Perry’s (2008)</td>
</tr>
<tr>
<td>Mass Transfer Coefficient</td>
<td>$k_{gi} = j_D N_{RE} N_{sc,j}^{1/3} \frac{D}{d_p}$</td>
<td>Croon and Halabi, 2008</td>
</tr>
<tr>
<td>Heat Transfer Coefficient</td>
<td>$h = j_{heat} \frac{C_p g \times mv}{N_{Pr}^{2/3}}$</td>
<td>Croon and Halabi, 2008</td>
</tr>
<tr>
<td>Peclet Number</td>
<td>$Pe = \frac{u_z L}{D_{eff}}$</td>
<td>Perry’s (2008)</td>
</tr>
</tbody>
</table>
Chapter 5: Results and Discussion

5.1 Reaction Kinetics

To determine the most practical rate law model, the parity plots were the first (1st) criterion used. For steam reforming, the power law yielded the best expression followed by Eley Rideal models. The average absolute deviation (AAD) for this reaction was 4–8.7 %. The productive ER models corresponded to the molecular adsorption of crude glycerol and surface reaction steps between the adsorbed intermediate and unadsorbed steam. Total Oxidation (TOR) had the best correlation for PLM but LHHW also gave AAD less than 20 %. Finally, CO2 Methanation had both PLM and ER for the adsorption of CO2 on the active site with an overall AAD for both models less than 20 %. After this, thermodynamic scrutiny was performed on the plausible mechanistic models.

5.1.1 Thermodynamic Scrutiny

The successful mechanistic models are subjected to a final criterion known as thermodynamic scrutiny. This regards the enthalpy and entropy of the system to analyze the thermodynamic consistency of the models. The most common thermodynamic scrutiny used is the Boudart-Mears-Vanice (BMV) rules and guidelines (Oluku et al. (2018), Halabi et al. (2010) and Praharso et al. (2004)). The Van’t Hoff equation is the basis for this thermodynamic scrutiny.

The correlation for the van’t Hoff equation is shown.

\[ \ln K_J = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \]  \hspace{1cm} (5.1)

\( \Delta S \) = Entropy \\
\( \Delta H \) = Enthalpy \\
R=Universal gas constant (J.mol/K).
The adsorption constant is given as:

\[ K_j = K_{j,o} \times \exp \left( -\frac{\Delta H_{f,ads}}{RT} \right) \]  \hspace{1cm} (5.2)

According to Praharso et al. (2004), Halabi et al., 2010 and Oluku et al. (2018), the benchmark to which the models were tested against are as shown below.

i. \[ \exp \left( \frac{S^0_j}{R} \right) = K_{j,o} < 1 \]  \hspace{1cm} (5.3)

ii. \[ K_{j,o} > \exp \left( \frac{S^0_j}{8.314} \right) \]  \hspace{1cm} (5.4)

iii. \[ \ln(K_{j,o}) \leq \frac{(12.2 - 0.0014\Delta H_{f,ads})}{8.314} \]  \hspace{1cm} (5.5)
Table 5-1: BMV Estimates for thermodynamic Scrutiny for Steam Reforming.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Correlation coefficient ($R^2$)</th>
<th>Criterion 1</th>
<th>Criterion 2</th>
<th>Criterion 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_1$ [J mol$^{-1}$]</td>
<td>$-8.01 \times 10^5$</td>
<td>0.78</td>
<td>$\Delta K_{f,1} &lt; 1$</td>
<td>$6.45 \times 10^{-47}$</td>
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<tr>
<td></td>
<td>$\Delta K_{f,3}$ [kPa$^{-1}$]</td>
<td>$6.45 \times 10^{-47}$</td>
<td></td>
<td></td>
<td>$&gt; 1.7 \times 10^{-11}$</td>
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<tr>
<td></td>
<td>$\Delta S_1$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-884.26</td>
<td></td>
<td></td>
<td>$-106.4$</td>
</tr>
<tr>
<td></td>
<td>$\Delta H_2$ [J mol$^{-1}$]</td>
<td>$-1 \times 10^6$</td>
<td>0.83</td>
<td>$\Delta K_{f,2} &lt; 1$</td>
<td>$9.23 \times 10^{-54}$</td>
</tr>
<tr>
<td></td>
<td>$\Delta K_{f,2}$ [kPa$^{-1}$]</td>
<td>$9.23 \times 10^{-54}$</td>
<td></td>
<td></td>
<td>$&gt; 1.4 \times 10^{-10}$</td>
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<tr>
<td></td>
<td>$\Delta S_2$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-1015.28</td>
<td></td>
<td></td>
<td>$-122$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\leq 169.86$</td>
</tr>
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<td></td>
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<td>$\Delta H_1$ [J mol$^{-1}$]</td>
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<td>$\Delta K_{f,1} &lt; 1$</td>
<td>$5.56 \times 10^{-9}$</td>
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<td></td>
<td>$\Delta K_{f,1}$ [kPa$^{-1}$]</td>
<td>$5.56 \times 10^{-9}$</td>
<td></td>
<td></td>
<td>$&gt; 1.7 \times 10^{-11}$</td>
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<tr>
<td></td>
<td>$\Delta S_1$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-158.03</td>
<td></td>
<td></td>
<td>$-19.01$</td>
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<td></td>
<td>$\Delta H_2$ [J mol$^{-1}$]</td>
<td>$-1.83 \times 10^5$</td>
<td>0.83</td>
<td>$\Delta K_{f,2} &lt; 1$</td>
<td>$3.73 \times 10^{-6}$</td>
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<td></td>
<td>$\Delta K_{f,2}$ [kPa$^{-1}$]</td>
<td>$3.73 \times 10^{-6}$</td>
<td></td>
<td></td>
<td>$&gt; 1.4 \times 10^{-10}$</td>
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<td></td>
<td>$\Delta S_2$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-103.91</td>
<td></td>
<td></td>
<td>$-12.5 \leq 1.47$</td>
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<tr>
<td>Model</td>
<td>Parameter</td>
<td>Correlation coefficient ($R^2$)</td>
<td>Criterion 1</td>
<td>Criterion 2</td>
<td>Criterion 3</td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
<td>---------------------------------</td>
<td>-------------</td>
<td>-------------</td>
<td>-------------</td>
</tr>
<tr>
<td>ER 4</td>
<td>$\Delta H_1$ [J mol$^{-1}$]</td>
<td>$-1.87 \times 10^5$</td>
<td>0.82</td>
<td>$\Delta K_{J,1} &lt; 1$</td>
<td>$-17.31 \leq 33$</td>
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<tr>
<td></td>
<td>$\Delta K_{J,1}$ [kPa$^{-1}$]</td>
<td>$3.01 \times 10^{-8}$</td>
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<tr>
<td></td>
<td>$\Delta S_1$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-143.98</td>
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<td></td>
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</tr>
<tr>
<td></td>
<td>$\Delta H_2$ [J mol$^{-1}$]</td>
<td>$-6.91 \times 10^4$</td>
<td>0.87</td>
<td>$\Delta K_{J,2} &lt; 1$</td>
<td>$-17.56$</td>
</tr>
<tr>
<td></td>
<td>$\Delta K_{J,2}$ [kPa$^{-1}$]</td>
<td>$2.35 \times 10^{-8}$</td>
<td></td>
<td>$2.35 \times 10^{-8}$</td>
<td>$-17.56 \leq 1.47$</td>
</tr>
<tr>
<td></td>
<td>$\Delta S_2$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-146.024</td>
<td></td>
<td>$&gt; 1.4 \times 10^{-10}$</td>
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</table>
Table 5-2: BMV Estimates for thermodynamic Scrutiny for Total Oxidation

<table>
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<tr>
<th>Model</th>
<th>Parameter</th>
<th>Correlation coefficient (R²)</th>
<th>Criterion 1</th>
<th>Criterion 2</th>
<th>Criterion 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHHW 2</td>
<td>$\Delta H_1$ [J mol$^{-1}$]</td>
<td>$-6.49 \times 10^4$</td>
<td>0.90</td>
<td>$\Delta K_{J,1} &lt; 1$</td>
<td>$-5.81 \times 10^{-9}$ $&gt; 1.7 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>$\Delta K_{J,1}$ [kPa$^{-1}$]</td>
<td>$-5.81 \times 10^{-9}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta S_1$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-157.67</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>$\Delta H_2$ [J mol$^{-1}$]</td>
<td>$-6.71 \times 10^{-4}$</td>
<td>0.71</td>
<td>$\Delta K_{J,2} &lt; 1$</td>
<td>$-4.43 \times 10^{-9}$ $&gt; 3.84 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$\Delta K_{J,2}$ [kPa$^{-1}$]</td>
<td>$-4.43 \times 10^{-9}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta S_2$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-159.92</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LHHW 6</td>
<td>$\Delta H_1$ [J mol$^{-1}$]</td>
<td>$-2.1004 \times 10^4$</td>
<td>0.86</td>
<td>$\Delta K_{J,1} &lt; 1$</td>
<td>$-2.5 \times 10^{-3}$ $&gt; 1.7 \times 10^{-11}$</td>
</tr>
<tr>
<td></td>
<td>$\Delta K_{J,1}$ [kPa$^{-1}$]</td>
<td>$-2.5 \times 10^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta S_1$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-49.73</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>$\Delta H_2$ [J mol$^{-1}$]</td>
<td>$-2.1007 \times 10^4$</td>
<td>0.86</td>
<td>$\Delta K_{J,2} &lt; 1$</td>
<td>$-1.51 \times 10^{-3}$ $&gt; 3.84 \times 10^{-9}$</td>
</tr>
<tr>
<td></td>
<td>$\Delta K_{J,2}$ [kPa$^{-1}$]</td>
<td>$-1.51 \times 10^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta S_2$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-53.98</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5-3: BMV Estimates for thermodynamic Scrutiny for CO2 Methanation

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameter</th>
<th>Correlation coefficient ($R^2$)</th>
<th>Criterion 1</th>
<th>Criterion 2</th>
<th>Criterion 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>ER 1</td>
<td>$\Delta H_1$ [J mol$^{-1}$]</td>
<td>$-2.93 \times 10^4$</td>
<td>0.71</td>
<td>$\Delta K_{J,1} &lt; 1$</td>
<td>$1.811 \times 10^{-3}$ ($&gt; 7.48 \times 10^{-12}$)</td>
</tr>
<tr>
<td></td>
<td>$\Delta K_{J,1}$ [kPa$^{-1}$]</td>
<td>$1.811 \times 10^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta S_1$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-52.49</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>$\Delta H_2$ [J mol$^{-1}$]</td>
<td>$-4.75 \times 10^4$</td>
<td>0.77</td>
<td>$\Delta K_{J,2} &lt; 1$</td>
<td>$3.89 \times 10^{-3}$ ($&gt; 1.52 \times 10^{-7}$)</td>
</tr>
<tr>
<td></td>
<td>$\Delta K_{J,2}$ [kPa$^{-1}$]</td>
<td>$3.89 \times 10^3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\Delta S_2$ [J mol$^{-1}$ K$^{-1}$]</td>
<td>-46.14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5-1: Van't Hoff plot for Steam Reforming Models.
Figure 5-2: Van't Hoff plot for Total Oxidation Models.
Figure 5-3: Van't Hoff plot for CO₂ Methanation

\[ y = -29280x + 1.8565 \]
\[ R^2 = 0.7734 \]

\[ y = -47491x + 7.5851 \]
\[ R^2 = 0.7115 \]
5.1.2 Comparison with Other Literature Studies

An activation energy comparison with available literature was done where the activation energy for the power law models is compared with available literature. A summary is given in the table 5-4 below. In the absence of heat and mass transfer resistances, the values of activation energy are $8.09 \times 10^4$, $8.7 \times 10^4$ and $8.86 \times 10^4$ for steam reforming, total oxidation and CO$_2$ methanation respectively. The reason for the variations may be attributed to experimental errors which includes the different experimental conditions like the S/C, O$_2$/C and Temperature ranges of 773-923K. Other contributing factors might be, the type of catalyst used, the flow rate and initial mole fraction of the reacting species present in the solution.
Table 5-4: Comparison of Various Studies for Power Law Kinetic Modelling of Individual Reactions

<table>
<thead>
<tr>
<th>Reforming Process</th>
<th>Catalyst</th>
<th>Temperature (K)</th>
<th>$E_a$ (J/mol)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Reforming</td>
<td>Ni/CeZrCa</td>
<td>773-923</td>
<td>$8.91 \times 10^4$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Ni/CeO₂</td>
<td>873</td>
<td>$10.34 \times 10^4$</td>
<td>Adhikari et al., 2011</td>
</tr>
<tr>
<td></td>
<td>Ni-ZrO₂/CeO₂</td>
<td>973</td>
<td>$4.34 \times 10^4$</td>
<td>Pant et al., 2011</td>
</tr>
<tr>
<td></td>
<td>Co-Ni/Al₂O₃</td>
<td>773-823</td>
<td>$6.33 \times 10^4$</td>
<td>Cheng et al., 2010</td>
</tr>
<tr>
<td>Total Oxidation</td>
<td>Ni/CeZrCa</td>
<td>773-923</td>
<td>$8.88 \times 10^4$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>N/A</td>
<td>N/A</td>
<td>$8.0 \times 10^4$ (pyrolysis)</td>
<td>Hemings et al., 2012</td>
</tr>
<tr>
<td></td>
<td>La₂O₃</td>
<td>773-873</td>
<td>$11.64 \times 10^4$ (Methane)</td>
<td>Nguyen et al., 2015</td>
</tr>
<tr>
<td>CO₂ Methanation</td>
<td>Ni/CeZrCa</td>
<td>773-923</td>
<td>$8.86 \times 10^4$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>La₂O₃</td>
<td>773-873</td>
<td>$8.78 \times 10^4$ (Methane)</td>
<td>Nguyen et al., 2015</td>
</tr>
<tr>
<td></td>
<td>Ni/(Al(O)ₓ</td>
<td>N/A</td>
<td>$9.36 \times 10^4$</td>
<td>Koschany et al., 2016</td>
</tr>
<tr>
<td></td>
<td>Ni/MgO</td>
<td>673-823</td>
<td>$8.79 \times 10^4$</td>
<td>Kathiraser et al., 2015</td>
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<tr>
<td></td>
<td>Ni/TiO₂</td>
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</tbody>
</table>
5.2 Reactor Modelling

Validation and comparison exercises between the developed models and experimental results were analyzed. The reactor validations and comparisons were done for the 1 dimensional and 2 dimensional models in MATLAB and COMSOL Multiphysics, respectively.

5.2.1 Reactor Validation

5.2.1.1 Validation of the MATLAB models

Predicted models from MATLAB were validated against the experimental work conducted by Ghani et al (2017). For the conversion validation, the absolute average deviation (AAD) was 9.99 % and 12.73 % for the 1-D PH and 1-D HET models respectively. Muthukumar et al. (2012) attributed the deviation of the predicted model from the experimental ones to the assumptions made (incompressible fluid and constant velocity). Additionally, the mole fraction was also validated with the experimental results. The absolute average deviation of the species are 10.54% and 11.61 % for H₂; 8.64% and 6.04% for CO₂; 3.67 % and 16.22 % for O₂; 9.05 % and 12.80 % for N₂ and 6.11 % and 8.43 % for CH₄. These values are for 1D PH and 1D HET models respectively. Pseudo homogeneous gave predictions closer to the experimental results than the heterogeneous model and a graphical presentation is shown in the figures 5-4 and 5-5.

5.2.1.2 Validation of COMSOL Multiphysics Models

For validation purposes, the reactor model developed by COMSOL Multiphysics was also validated against the experimental work conducted by Ghani et al (2017). The maximum absolute average deviation (AAD) between the conversions was 12.08 % and 13.12 % for the 2D PH and 2D HET models respectively. The variation may be as a consequence of
the assumptions (incompressible fluid and constant velocity) made for the models which may have caused the under and over predictions of some parameters (Muthukumar et al., 2012).

Besides the validation with the experimental conversion with the models, the mole fraction of the species was also validated with experimental ones. The error or deviation of the experimental against predicted mole fraction varied per the species under consideration. \( \text{H}_2 \) was 11.62\% and 20.08\%; \( \text{CO}_2 \) was 18.2\% and 32.61\%; \( \text{O}_2 \) was 7.66\% and 16.16\%; \( \text{N}_2 \) was 3.86\% and 3.34\% and \( \text{CH}_4 \) was 6.62\% and 0.63\% for 2D PH and 2D HET models respectively. From the error, it could be seen that the numerical solution over predicted \( \text{CO}_2 \) and \( \text{N}_2 \) whilst it under predicted \( \text{H}_2 \) as seen in figure 5-6. 2D Pseudo homogeneous gave closer predictions of the experimental results than the 2D heterogeneous model.

During the validation of the models, it could be seen that, all models underpredicted the conversion for 0.42-0.56 and 0.8-1.0 whereas almost all the models were well aligned with the experimental ones between a range of 0.58-0.8. It could be that, the assumptions made for the numerical model at the early stages and exit deviated slightly from the experimental ones. In addition, the conversion from the experimental work was higher at the inlet conditions for the experimental work than it was for the numerical. Thus, the numerical model is better at predicting the conversion of the experiments between a range of 0.58-0.8.
Figure 5-4: Parity plot of Experimental Conversion against Predicted Conversion for MATLAB Models
Figure 5-5: Parity plot of Experimental Conversion against Predicted Conversion for COMSOL Models.
<table>
<thead>
<tr>
<th>Species</th>
<th>Absolute Average Deviation (AAD)</th>
<th></th>
</tr>
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<tr>
<td></td>
<td>1 D PH (%)</td>
<td>1D HET (%)</td>
</tr>
<tr>
<td>O₂</td>
<td>3.7</td>
<td>16.2</td>
</tr>
<tr>
<td>N₂</td>
<td>9.1</td>
<td>12.8</td>
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<tr>
<td>CO₂</td>
<td>8.6</td>
<td>6.0</td>
</tr>
<tr>
<td>H₂</td>
<td>10.5</td>
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</tr>
<tr>
<td>CH₄</td>
<td>6.1</td>
<td>8.4</td>
</tr>
</tbody>
</table>
5.2.2 Reactor Comparison

A comparison was made between the two models developed in both MATLAB and COMSOL Multiphysics. The result is as shown in graphs below. Parameters such as Temperature, mole fraction and conversion amongst other parameters were intensively analyzed for each model. For the 1-D model comparison made by MATLAB, there is negligible difference between the mole fractions of species. The only difference seen from the comparison was in the temperature profile. The HET model was about 20 K greater than the PH model. This difference is aligned with that found in Halabi and Croon, 2008 and Lordanidis, 2002. According to Lordanidis (2002), assuming the bulk gas and spherical catalyst have the same conditions, the actual rate deviates less than 5% from the calculated rate provided equation 5.6 is met.

\[
\frac{R d_p}{kT} (5.23 \times 10^{-9}) < 0.15 \frac{dT}{E} (1.86 \times 10^{-5})
\]

The exact deviation between the PH and HET model is accounted for by

\[
Deviation = \frac{R_{(HET)} - R_{(PH)}}{R_{(HET)}}
\]

The main difference in the temperature of the 1D models stems from the heat and mass transfer across the interface. Based on the reactions occurring with respect to the catalyst, the HET model has a higher temperature than the PH due to the reaction rate which is greatly responsive to temperature. Also, the extra heat generated from the reactions, both fluid and solid phases are expected to have a higher Temperature than PH whilst the concentration profiles generated very similar trends.

The 2-D models developed in COMSOL showed a slight difference between the two (2) models when compared. This difference could be attributed to the axial dispersion model
used in MATLAB as against no axial dispersion model in COMSOL. The difference in temperature profile was observed to have the same trend as in the 1 D models. The reaction rate is high close to the entrance of the reactor due to the concentrated number of reactants at the inlet that the exit. The exothermic reactions taking place may have contributed to the high temperature seen at the entrance region than at the rear section which was almost flat due to the existence of endothermic reactions. The heat produced by the exothermic reactions was used by the endothermic reaction and the overall ATR process was sustained, as such, there was no substantial decrease in temperature at the outlet.

From the figure 5-11, the conversions of the various models were compared the order is as shown below:

\[ X_{2D \text{HET}} > X_{2D \text{PH}} > X_{1D \text{PH}} > X_{1D \text{HET}} \]

When the conversions were compared, it was seen that the conversion was greatest in 2D HET followed by 2D PH, 1D PH with the least being 1D HET. This could be because of the additional terms added to the 2D models which enhances mixing of reactants and increases the conversion. In addition, the difference between the 2D models and 1D ones lie in the assumptions made in the models. Also, from figure 5-10, it could be seen that all models predict the exit conversion with no significant difference between them. Thus, it could be said that all models align well with the exit conversion. The difference between the models as seen between 0-0.2 m could be as a result of the different assumptions used for the 1 and 2D models and also, the no update of thermophysical properties in the 2D models as against that in the 1D models. Finally, from figure 5-12, it could be seen that there is no significant variation in concentration in the radial direction for the 2D models. Hence, a 1 D model is sufficient to model the ATR process of crude glycerol.
Figure 5-6: Comparison of PH and HET Models for 1-D Models in MATLAB
Figure 5-7: Temperature and Mole fraction Graphs for 1-D models
Figure 5-8: Comparison of PH and HET Models for 2-D Models in COMSOL.
Figure 5-9: Temperature and Mole fraction Graphs for 2-D models
Figure 5-10: Conversion Comparison of all models

Figure 5-11: Variation in mole fraction of species across the reactor length.
Even though 2 D HET yielded the best conversion along the reactor, 1 D PH model gave better validation results for both mole fractions and conversion. In addition to this, there was no variation in the mole fraction along the radial direction as seen in figure 9.8.

5.2.3 Effects of Temperature

Temperature is an important factor that favors the kinetics of the system. From figure 5.17, it could be seen that at a particular space time, increasing the temperature increases the conversion of the system. According to Uwem et al., 2017, to achieve thermoneutral conditions for autothermal reforming of crude glycerol, the optimum conditions of S/C=2.6 with an adiabatic temperature of 923 K yields maximum hydrogen. According to figure 5-18, it could be seen that the maximum conversion was obtained at 923 K and the equilibrium conversion was higher than the conversion far from equilibrium with a maximum conversion of 0.99.

5.2.4 Effects of Axial Dispersion

Axial dispersion has negligible effects on the mass fraction of the species as seen in figure 5-13. The graph shows the exit mass fraction for the species under consideration. This can be attributed to the plug flow criterion (L/d_p >50). Also, at steady state, there complete mixing and the plug flow condition also ensures no back mixing. Thus, little to no variation is seen in the profiles. Conversion also showed no significant variation at equilibrium. Figure 5-14 shows axial dispersion variation for temperature along the reactor length and the temperature profiles produces similar results whereas for the species mass fraction, the axial dispersion model produces quite higher results. The overall AAD is 0.14 % which shows the negligible effects of this parameter in this work.
Figure 5-12: Effects of Axial Dispersion on Exit Mass Fraction

Figure 5-13: Effects of Axial Dispersion on Temperature
5.2.5 Effects of W/FAO on Reactor Performance

The overall aim of reactor design is to enhance its performance. In this work, the performance is analyzed in terms of conversion and yield. Increasing the space time from figure 5-15 indicates an increase in both yield and conversion. In the experimental work, the effects of space time were analyzed at a variable catalyst weight of 0.025-0.25 g. The space times used were 12.71, 50.94.76.47 and 101.94 gcatmin/mol with associated conversions of 38 %, 59%, 73% and 88%. In fact, at the entrance of the reactor, a sharp increase in conversion and yield which was seen at the first 45 % of the reactor length was followed by a gentle increase in the remaining 55 %. At a reactor length of 0.025 m, about 93 % of the conversion and yield had been obtained and thus only 7 % more conversion and yield could be achieved by the remaining 0.02 m.

5.2.6 Effects of Reactor Length on Conversion

In solid catalyzed reactions, another way of increasing the performance of the reactor model is to increase the contacting surface area and the space time. This can be done by increasing the reactor length. The longer the reactor, the more the amount of catalyst needed to fill the reactor. The more the catalyst, the higher the contacting surface and the higher the performance since more reactions can occur. Contrary in figure 5-16, the reactor length was varied between 45-100 mm where the length of 100 mm gave a conversion of 90 % as against 75 mm which was 88 % and finally 45 mm as 84 %. It has also been established from 5-15 that a greater percentage of the conversion occurs at about 45 % of the reactor length thus, an additional conversion of 6 % is not substantial enough compared to the huge amount of money which will be used to purchase more catalyst for a longer reactor.
Figure 5-14: Effects of W/F_{AO} on Reactor Performance
Figure 5-15: Effects of Reactor Length on Performance

Figure 5-17: Effects of Temperature on Conversion at W/FAO of 12.71 gcatmin/mol
Figure 5-16: Effects of equilibrium conversion on temperature.
Chapter 6: Limitations, Conclusions and Recommendations

6.1 Limitations

- The use of a constant effectiveness factor may have introduced some errors into the models. This is because the effectiveness factor is a function of concentration which varies along the reactor length.
- Constant transport properties in COMSOL Multiphysics as well as the assumption of incompressible fluid in MATLAB models may have contributed some errors to the results. In totality, the results generated by the numerical model are aligned to the experimental results after performing validation exercise.
- Kinetics over steam to carbon ratio (S/C) of 2.6 and Oxygen to Carbon ratio (O₂/C) of 0.125 is not enough to fully study and comprehend the kinetics of crude glycerol autothermal reforming process.

6.2 Conclusions

The intrinsic kinetics of crude glycerol autothermal reforming (ATR) was studied over Ni/CeZrCa catalyst in a temperature range of 773-23 K, 1 atm pressure, S/C ratio of 2.6 and O₂/C of 0.125. The intrinsic kinetic data provided by Ghani et al. (2017) was not limited by heat and mass transfer and the conditions were assumed to be far from equilibrium. The kinetics was studied using the Arrhenius Power law rate model and the mechanistic kinetics which was basically done using Langmuir Hinshelwood Hougen-Watson (LHHW) and Eley Rideal (ER) approach.

For steam reforming, ER model best describes the rate. The successful models were the adsorption of crude glycerol on the active site and the surface reaction steps. ER 4 was
chosen as the ultimate model after the thermodynamic scrutiny with an AAD of less than 10%. This corresponds to the surface reaction between the adsorbed intermediate and steam.

The best kinetics for total oxidation was described by the power law model. For the mechanistic aspect, LHHW approach yielded successful models comparative to ER. The mechanistic model that describes the TOR process was the molecular adsorption of crude glycerol with an AAD of 14.6%.

Finally, CO₂ Methanation was the final reaction considered. The kinetics was best described by the ER mechanism for the adsorption of carbon dioxide (CO₂). This model yielded an AAD of 5.8%. There was no kinetic data on CO thus, the water gas shift reaction was not considered in this study. The resulting models for this study are thermodynamically consistent and statistically accurate.

Numerical modelling for crude glycerol autothermal reforming was also studied using COMSOL Multiphysics 5.2 and MATLAB 2017. Both one (1) and two (2) dimensional reactor models were developed based on pseudo homogenous and heterogeneous models. Kinetics developed in this work was incorporated in the numerical model and the results were validated against experimental work. The average absolute deviations obtained for the one (1) dimensional model were 10 % and 12.73 % for pseudo homogenous and heterogeneous model respectively. For the 2 –dimensional models, an AAD of 12.08 % for pseudo homogeneous and 13.1 % for heterogeneous. There was a negligible effect of process parameters in the radial direction. Based on the above, an inference that, a 1-dimensional model is enough to accurately model a 12.7 mm by 45 mm reactor.
6.3 Recommendations

- Test all kinetic models in numerical modelling. Both the power law and mechanistic models should be incorporated in the developed in-house code to observe the full effects of kinetics on the reactor design. This model makes use of the power law model. This will give better understanding of the ATR process for crude glycerol.

- A broader kinetic data should be made available to expand the conditions for the mechanistic models and make it more applicable over a range of steam to carbon ratio (S/C) of 2.6 and Oxygen to Carbon ratio (O₂/C).

- Variable transport properties with temperature and effectiveness factor should be incorporated in the model to enhance better results.
References


Geankoplis, C. J. (2003). In Geankoplis C. J., Safari Tech Books Online (Eds.), *Transport processes and separation process principles (includes unit operations)* Place of publication not identified Prentice Hall PTR.


Halabi, M. H. *Sorption enhanced catalytic reforming of methane for pure hydrogen production: Experimental and modeling* doi:DOI: 10.6100/IR709035


Appendix

Appendix-A: Experimental Data and Supplementary Kinetic Information

1. Experimental Data Used

<table>
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<tr>
<th>W/FAO, (gcat.min/molC)</th>
<th>T/K</th>
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<th>pB</th>
<th>pC</th>
<th>X exp</th>
<th>AAD</th>
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<td>0.61</td>
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2. Kinetic Model Developments

1. Steam Reforming Mechanism

A. Eley Rideal Model

In this case, it is assumed that only one reactant was adsorbed on a site and the other stays in the gas phase (Fogler, 1999). For the sake of simplicity, crude glycerol is assumed to be pure glycerol and represented as

\[ A + 3 \, B \rightarrow 3 \, E + 7 \, F \]  \hfill (A.1)

\[ 0.8 \, A + 2.4 \, B \leftrightarrow 2 \, E + 5.2 \, F \]  \hfill (A.1a)

- Adsorption of crude glycerol on active site

\[ A + S \rightarrow A_S \]  \hfill (A.2)

- Dissociation of adsorbed intermediate on a vacant site to form two (2) different oxygenated hydrocarbon compounds (ethylene glycol and formaldehyde).

\[ A_S + S \rightarrow H_S + I_S \]  \hfill (A.3)

- Surface Reaction between adsorbed intermediate and non-adsorbed steam in the bulk gas

\[ H_S + 2.2 \, B \rightarrow 1.5 \, E + 4.2 \, F + S \]  \hfill (A.4)

\[ I_S + 0.2 \, B \rightarrow 0.5 \, E + F + S \]  \hfill (A.5)

Assuming all reactions are reversible

The equilibrium expression for each of these four (4) reactions can be given as
\[ K_{eq,1} = \frac{[A.S]}{[A]^{0.8}[S]} \]  
(A.6)

\[ K_{eq,2} = \frac{[H.S][I.S]}{[A.S]} = \frac{[F]^{5.2}[E][S]^2}{K_{eq,3}K_{eq,4}[B]^{2.4}} \]  
(A.7)

\[ [A.S] = \frac{[F]^{5.2}[E][S]^2}{K_{eq,2}K_{eq,3}K_{eq,4}[B]^{2.4}} \]  
(A.7a)

\[ K_{eq,3} = \frac{[F]^{4.2}[E]^{1.5}[S]}{[1.5][B]^{2.2}} \]  
(A.8)

\[ K_{eq,4} = \frac{[F][E]^{0.5}[S]}{[2.5][B]^{0.2}} \]  
(A.9)

Using equation (1) as RDS, the rate law is

\[ r_1 = k_{1f}[A]^{0.8}[S] - k_{1r}[A.S] \]  
(A.10)

Dividing 5.5 through by \( k_{1f} \) and substituting 5.2a into the equation

\[ r_1 = k_{01}e^{-\frac{E_1}{RT}} \times \left( [A]^{0.8}[S] - \frac{[F]^{5.2}[E][S]}{K_{1(eq)K_{eq,2}K_{eq,3}K_{eq,4}[B]^{2.4}}} \right) \]  
(A.11)

\[ K_{1(eq)K_{eq,2}K_{eq,3}K_{eq,4}} = K_p \]  
(A.12)

The only parameter we do not have data for is the parameter \( S \) for active site and hence, it is represented by \( St \) which is the total number of sites

\[ St=S+[A.S] + [I.S] + [H.S] \]  
(A.13)

\[ St=S+\frac{[F][E]^{0.5}}{K_{eq,4}[B]^{0.2}} + \frac{[F]^{4.2}[E]^{1.5}}{K_{eq,3}[B]^{2.2}} + \frac{[F]^{5.2}[E]^2}{K_{eq,2}K_{eq,3}K_{eq,4}[B]^{2.4}} \]  
(A.13a)

\[ St=S\left(1 + \frac{[F][E]^{0.5}}{K_{eq,4}[B]^{0.2}} + \frac{[F]^{4.2}[E]^{1.5}}{K_{eq,3}[B]^{2.2}} + \frac{[F]^{5.2}[E]^2}{K_{eq,2}K_{eq,3}K_{eq,4}[B]^{2.4}} \right) \]  
(A.13b)

\[ K_B = \frac{1}{K_{eq,4}}; \quad K_A = \frac{1}{K_{eq,3}}; \quad K_F = \frac{1}{K_{eq,2}K_{eq,3}K_{eq,4}} \]  
(A.13c)

\[ k_1 = k_{01}e^{-\frac{E_1}{RT}St} \]  
(A.13d)

Substitute A.13 c into A.14

\[ r_1 = k_1 \times \left( [A]^{0.8}[S] - \frac{[F]^{5.2}[E][S]}{K_{1(eq)K_{eq,2}K_{eq,3}K_{eq,4}[B]^{2.4}}} \right) \]  
(A.14)
\[
 r_1 = k_0 e^{-(\frac{E_1}{RT})} \times \left[ \frac{([A]^{0.8} - \frac{[E]^2[F]^{5.2}}{K_{p(eq)}(B)^{2.4}})}{1 + \frac{K_F[E]^2[F]^{5.2}}{(B)^{2.4}} + \frac{K_B[F][E]^{0.5}}{(B)^{0.2}} + \frac{K_A[E]^{1.5}[F]^{4.2}}{(B)^{2.2}}} \right] \quad (A.15)
\]

Using (2) as rds, the same approach is followed and summarized in the table below

- Dissociation of adsorbed intermediate on a vacant site to form two (2) different oxygenated hydrocarbon compounds (ethylene glycol and formaldehyde).

\[
 A.S+S \rightarrow HS+IS \quad \text{(A.3)}
\]

Using equation (A.3) as RDS, the rate law is

\[
 r_2 = k_{2f} [A.S][S] - k_{2r}[H.S][I.S] \quad \text{(A.16)}
\]

\[
 k_2 = k_{02} e^{-(\frac{E_2}{RT})} St \quad \text{(A.17)}
\]

\[
 r_2 = k_2 \times \left( K_{eq,1}[A]^{0.8}[S][S] - \frac{[F]^{5.2}[E]^2[S][S]}{K_{eq,2}K_{eq,3}K_{eq,4}(B)^{2.4}} \right) \quad \text{(A.18)}
\]

\[
 r_2 = k_2 K_{eq,1} \times \left( [A]^{0.8}[S][S] - \frac{[F]^{5.2}[E]^2[S][S]}{K_{eq,2}K_{eq,3}K_{eq,4}(B)^{2.4}} \right) \quad \text{(A.19)}
\]

\[
 K_{1(eq)} K_{eq,2} K_{eq,3} K_{eq,4} = K_p \quad \text{(A.20)}
\]

The only parameter we do not have data for is the parameter S for active site. Thus, it is represented by St which is the total number of sites

\[
 St=S+[A]^{0.8} + [H1.S] + [I.S] \quad \text{(A.21)}
\]

\[
 St=S+\frac{[F][E]^{0.5}}{K_{eq,4}(B)^{0.2}} + \frac{[F]^{4.2}[E]^{1.5}}{K_{eq,3}(B)^{2.2}} + K_{eq,1}[A]^{0.8} \quad \text{(A.21a)}
\]

\[
 St=S\left(1 + K_{eq,1}[A]^{0.8} + \frac{[F]^{4.2}[E]^{1.5}}{K_{eq,3}(B)^{2.2}} + \frac{[F][E]^{0.5}}{K_{eq,4}(B)^{0.2}} \right) \quad \text{(A.21b)}
\]

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\[ K_B = \frac{1}{K_{eq,4}}; \quad K_A = K_{eq,1} ; \quad K_W = \frac{1}{K_{eq,3}} \]  
(A.21 c)

Substitute A.21 c. into A.22

\[ r_2 = k_0 e^{-\left(\frac{E_3}{RT}\right)} \times \left[ \frac{[A]^{0.8} \cdot [E]^{2.52} \cdot [F]^{2.4}}{K_{p2(eq)} [B]^{2.4}} \right] \left[ 1 + K_A [A]^{0.8} + K_B [E]^{0.5} + K_W [E]^{1.5} [F]^{4.2} \right] \]  
(A.22)

Using (3) as RDS

\[ H.S + 2.22B \rightarrow 1.5E + 4.2F + S \]  
(A.4)

\[ r_3 = k_3 f [H.S][B]^2 - k_3 r [E]^{1.5} [F]^{4.2} [S] \]  
(A.23)

From equilibrium constant equation (A.21)

\[ [A2.S] = \frac{K_{eq,1} K_{eq,2} K_{eq,4} [A]^{0.8} [B]^{2.4}}{[F] [E]^{0.5}} \]  
(A.24)

\[ r_3 = k_3 \times \left( \frac{K_{eq,1} K_{eq,2} K_{eq,4} [A]^{0.8} [B]^{2.4} [S]}{[F] [E]^{0.5}} - \frac{[E]^{1.5} [F]^{4.2} [S]}{K_{eq,3}} \right) \]  
(A.25)

\[ r_3 = k_3 \times K_{eq,1} K_{eq,2} K_{eq,4} K_{eq,3} \times \left( \frac{[A]^{0.8} [B]^{2.4} [S]}{[F] [E]^{0.5}} - \frac{[E]^{1.5} [F]^{4.2} [S]}{K_{eq,3}} \right) \]  
(A.26)

\[ K_{1(eq)} K_{eq,2} K_{eq,3} K_{eq,4} = K_p \]  
(A.27)

\[ K_{1(eq)} K_{eq,2} K_{eq,3} K_{eq,4} St = k_{03} e^{-\left(\frac{E_3}{RT}\right)} \]  
(A.27 a)

The only parameter we do not have data for is the parameter S for active site. Thus, it is represented by St which is the total number of sites

\[ St = S + [A.S] + [H.S] + [I.S] \]  
(A.28 a)
\[ \text{St} = S \left( 1 + K_{eq,1}[A]^{0.8} + \frac{K_{eq,1}K_{eq,2}K_{eq,4}[A]^{0.8}[B]^{2.4}}{[E]^{1.5}[F]^{4.2}} + \frac{[E][F]^2}{K_{eq,4}[B]} \right) \quad (A.28 \text{ b}) \]

\[ K_B = \frac{1}{K_{eq,4}}; \quad K_A = K_{eq,1}; \quad K_Q = K_{eq,1}K_{eq,2}K_{eq,4} \quad (A.28 \text{ c}) \]

Substitute A.28 c into A.25

\[ r_3 = k_{03}e^{-\frac{E_3}{RT}} \times \left[ \frac{\left( [A]^{0.8}[B]^{2.4} - [E]^{1.5}[F]^{4.2} \right)}{K_{p,3}} \right] \left( 1 + K_A[A]^{0.8} + \frac{K_Q[A]^{0.8}[B]^{0.2}}{[F][E]^{0.5}} + \frac{K_B[F][E]^{0.5}}{[B]^{0.2}} \right) \quad (A.29) \]

Using (4) as RDS: \( I.S + 0.2B \rightarrow 0.5E + F + S \) \quad (A.5)

\[ r_4 = k_{4f}[I.S][B] - k_{4r}[E][F]^2[S] \quad (A.30) \]

\[ r_4 = k_{04}e^{-\frac{E_4}{RT}} \times \left[ \frac{\left( [A]^{0.8}[B]^{2.4} - [E]^{0.5}[F]^{1.0} \right)}{K_{4(eq)}} \right] \left( 1 + K_A[A]^{0.8} + \frac{K_{4A}[E]^{1.5}[F]^{4.2} + K_{4(ads)}[A]^{0.8}[B]^{2.2}}{[B]^{2.2} + \left( [E]^{1.5}[F]^{4.2} \right)} \right) \quad (A.31) \]
Appendix-B: Equilibrium Conversion

Equilibrium Constant

The equation is given by

A + 0.75B + 0.625C ⇌ 2D + 0.5E + 3.25F  \hspace{1cm} (B.1)

To get the Gibbs free energy and heat of formation of the crude glycerol, the table below shows it.

Equilibrium constant Kp Calculation

\[ -\ln(K_P) = \frac{\Delta G}{RT} \]  \hspace{1cm} (B.2)

<table>
<thead>
<tr>
<th>Species</th>
<th>(\Delta H_f) [kJ/mol]</th>
<th>(\Delta G_f) [kJ/mol]</th>
<th>(\Omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3H8O3</td>
<td>-669.6</td>
<td>-478.6</td>
<td>0.591</td>
</tr>
<tr>
<td>O2</td>
<td>0</td>
<td>0</td>
<td>0.021</td>
</tr>
<tr>
<td>H2O</td>
<td>-242</td>
<td>-228.8</td>
<td>0.344</td>
</tr>
<tr>
<td>H2</td>
<td>0</td>
<td>0</td>
<td>-0.216</td>
</tr>
<tr>
<td>CO2</td>
<td>-393.8</td>
<td>-394.6</td>
<td>0.225</td>
</tr>
<tr>
<td>N2</td>
<td>0</td>
<td>0</td>
<td>0.039</td>
</tr>
<tr>
<td>CH4</td>
<td>-74.9</td>
<td>-50.87</td>
<td>0.011</td>
</tr>
</tbody>
</table>

\[ K = \exp\left(\frac{-\Delta G^0}{RT}\right) = \prod_i a_i^{v_i} \]

Faria et al., 2013

<table>
<thead>
<tr>
<th>Species</th>
<th>(H_f) [kJ/mol]</th>
<th>(G_f) [kJ/mol]</th>
<th>(v_j)</th>
<th>(\Delta H_f) [kJ/mol]</th>
<th>(\Delta G_f) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3H8O3</td>
<td>-669.6</td>
<td>-478.6</td>
<td>1</td>
<td>478.6</td>
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<tr>
<td>O2</td>
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<tr>
<td>H2O</td>
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<td>H2</td>
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<tr>
<td>CO2</td>
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<td>-394.6</td>
<td>2</td>
<td>-789.2</td>
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<tr>
<td>N2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>CH4</td>
<td>-74.9</td>
<td>-50.87</td>
<td>0.5</td>
<td>-25.435</td>
<td>-164.435</td>
</tr>
</tbody>
</table>
\[-\ln(K_p) = \frac{\Delta G}{RT} = \frac{\Delta G_0^\circ}{RT_i} + \frac{\Delta H_0^\circ}{RT_i} \int_0^{T_i} \frac{\Delta C_P}{R} + \int_0^{T_F} \frac{\Delta C_P}{RT_F}\]

<table>
<thead>
<tr>
<th>Species</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3H8O3</td>
<td>9.656</td>
<td>4.283E-01</td>
<td>-2.68E-04</td>
<td>3.18E-08</td>
<td>2.77E-11</td>
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<tr>
<td>O2</td>
<td>29.526</td>
<td>-8.99E-03</td>
<td>3.81E-05</td>
<td>-3.26E-08</td>
<td>8.86E-12</td>
</tr>
<tr>
<td>H2O</td>
<td>33.933</td>
<td>-8.42E-03</td>
<td>2.99E-05</td>
<td>-1.78E-08</td>
<td>3.69E-12</td>
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<tr>
<td>H2</td>
<td>25.399</td>
<td>2.0178E-02</td>
<td>-3.85E-05</td>
<td>3.19E-08</td>
<td>-8.76E-12</td>
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<tr>
<td>CO2</td>
<td>27.437</td>
<td>4.23E-02</td>
<td>-1.96E-05</td>
<td>3.997E-09</td>
<td>2.99E-13</td>
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<tr>
<td>N2</td>
<td>29.342</td>
<td>-3.54E-03</td>
<td>1.0076E-05</td>
<td>-4.31E-09</td>
<td>2.59E-13</td>
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<tr>
<td>CH4</td>
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<td>-3.996E-02</td>
<td>1.92E-04</td>
<td>-1.53E-07</td>
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<tr>
<td>(\Delta)</td>
<td>101.0208</td>
<td>-0.2874</td>
<td>1.5590e-04</td>
<td>3.5424e-08</td>
<td>-4.5022e-11</td>
</tr>
</tbody>
</table>

All constants are in J/molK

\[-\ln(K_p) = \frac{\Delta G}{RT} = \frac{-164435}{8.314+773}\]

\[K_p = 1.29 \times 10^{11} \text{ at } 773 \text{ K}\]

\[K_p = 2.734 \times 10^{10} \text{ at } 823 \text{ K}\]

The equilibrium expression is

\[
\frac{[y_{H_2}]^{3.25} \times [\varphi_{H_2}]^{3.25} [y_{CO_2}]^2 \times [\varphi_{CO_2}]^2 [y_{CH_4}]^{0.5} \times [\varphi_{CH_4}]^{0.5}}{[y_{H_2O}]^{0.75} \times [\varphi_{H_2O}]^{0.75} [y_{O_2}]^{0.65} \times [\varphi_{O_2}]^{0.65} \times [y_{C_3H_8O_3}] \times [\varphi_{C_3H_8O_3}]} = K_p \left(\frac{P}{P_0}\right)^{\sum_{j=1}^{n} v_j}
\]

\[\varphi = \text{ activity coefficient}\]

\[\varphi = \exp\left(\frac{P_r}{T_r (\beta_0 + \omega \beta_1)}\right)\]

\[\beta_0 = 0.083 - \frac{0.422}{(T_r)^{1.6}}\]
\[ \beta_1 = 0.139 - \frac{0.172}{(T_r)^{4.2}} \]

\[ \nu = \nu_{\text{product}} - \nu_{\text{reactant}} \]

\[ \nu = 6.15 \]

Thermodynamic data, Smith et al. (1996); Akande, 2006; Prausnitz et al.,

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Omega )</th>
<th>( T_c )</th>
<th>( T_r )</th>
<th>( P_c )</th>
<th>( P_r )</th>
<th>( \beta_0 )</th>
<th>( \beta_1 )</th>
<th>( \varphi )</th>
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<tr>
<td>C3H8O3</td>
<td>0.5</td>
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<td>850</td>
<td>0.909411</td>
<td>765</td>
<td>0.013333</td>
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<td>796</td>
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<td>CO2</td>
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<td>304</td>
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<td>0.013550</td>
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<td>0.021739</td>
<td>13</td>
<td>0.038157</td>
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<td>.4</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>

\[ \frac{[y_{H_2}]^{3.25} \times [\varphi_{H_2}]^{3.25} [y_{CO_2}]^{2} \times [\varphi_{CO_2}]^{2} [y_{CH_4}]^{0.5} \times [\varphi_{CH_4}]^{0.5} \times [y_{H_2O}]^{0.75} \times [\varphi_{H_2O}]^{0.75} [y_{O_2}]^{0.65} \times [\varphi_{O_2}]^{0.65} \times [y_{C_3H_8O_3}] \times [\varphi_{C_3H_8O_3}]}{[y_{H_2O}]} = K_p * 1 \ldots \ldots (B1) \]

For equilibrium

Total moles = 6.15 + 6.15 Xe
\[ y_{H_2} = \frac{3.25 \text{Xe}}{6.15 + 6.15 \text{Xe}} \]
\[ y_{CO_2} = \frac{2 \text{Xe}}{6.15 + 6.15 \text{Xe}} \]
\[ y_{CH_4} = \frac{0.5 \text{Xe}}{6.15 + 6.15 \text{Xe}} \]
\[ y_{H_2O} = \frac{0.75 - 0.75 \text{Xe}}{6.15 + 6.15 \text{Xe}} \]
\[ y_{O_2} = \frac{0.65 - 0.65 \text{Xe}}{6.15 + 6.15 \text{Xe}} \]
\[ y_{C_3H_8O_3} = \frac{1 - \text{Xe}}{6.15 + 6.15 \text{Xe}} \]

Putting the above into equation in equation B1 and simplifying it further, the equation becomes

\[
\frac{7.5725 \text{Xe}^3}{-0.4875 \text{Xe}^3 - 0.4875 \text{Xe}^2 - 1.4625 \text{Xe} + 2.162} = 1.29 \times 10^{11}
\]

This cubic equation is simplified to obtain,

\[
6.287 \times 10^{10} \text{Xe}^3 + 6.287 \times 10^{10} \text{Xe}^2 + 1.89 \times 10^{11} \text{Xe} - 2.789 \times 10^{11} = 0
\]

Real and imaginary roots are obtained for the above quadratic and the real root is

\[ \text{Xe} = 0.93 \]

Thus, the equilibrium conversion is 0.93.

At 823;

<table>
<thead>
<tr>
<th>Specie</th>
<th>( \Omega )</th>
<th>( T_c )</th>
<th>( T_r )</th>
<th>( P_c )</th>
<th>( P_r )</th>
<th>( \beta_0 )</th>
<th>( \beta_1 )</th>
<th>( \phi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3H8O3</td>
<td>0.5</td>
<td>850</td>
<td>0.968235</td>
<td>91</td>
<td>0.013333</td>
<td>-874</td>
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<td>0.965791</td>
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<td></td>
<td>91</td>
<td>294</td>
<td>333</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>706</td>
</tr>
</tbody>
</table>
Putting the above into equation in equation B1 and simplifying it further, the equation becomes

\[
\frac{3.25 Xe^3 \times 1.849}{(-0.4875Xe^3 - 0.4875Xe^2 - 1.4625Xe + 0.7211) \times 0.993} = 2.734 \times 10^{10}
\]

\[
\frac{6.01 Xe^3}{(-0.4875Xe^3 - 0.4875Xe^2 - 1.4625Xe + 1.951)} = 2.715 \times 10^{10}
\]

This cubic equation is simplified to obtain,

\[1.3236 \times 10^{10}Xe^3 + 1.3236 \times 10^{10}Xe^2 + 3.9708 \times 10^{10}Xe - 5.2972 \times 10^{10} = 0\]

Real and imaginary roots are obtained for the above quadratic and the real root is

\[Xe=0.87\]

Thus, the equilibrium conversion is 0.87.

Increase in temperature reduces the equilibrium conversion and that, high conversion of 0.93 was seen at temperature of 773 K than at 823 K (0.87).
Appendix-C: Graphical Presentation of mole fraction validation

![Validation of Species Distribution](image1)

![Validation of Species Distribution](image2)

Figure C-0-1: Species validation for both 1-D and 2-D Models.
Figure C 1: Effects of Mole Fraction in Temperature Profile for 1D PH model
## Appendix-D: Parameters for Numerical Modelling

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
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<td>$\Lambda$</td>
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<td>W/mK</td>
</tr>
<tr>
<td>$C_p$</td>
<td>2.02</td>
<td>kJ/kgK</td>
</tr>
<tr>
<td>$L$</td>
<td>0.045</td>
<td>m</td>
</tr>
<tr>
<td>$D$</td>
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<td>m</td>
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<td>$d_p$</td>
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<td>mm</td>
</tr>
<tr>
<td>$\varepsilon_p$</td>
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</tr>
<tr>
<td>FAO</td>
<td>$3.17 \times 10^{-5}$</td>
<td>mol/s</td>
</tr>
<tr>
<td>$M_{\text{avg}}$</td>
<td>26.24</td>
<td>kg/kmol</td>
</tr>
<tr>
<td>$T_0$</td>
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<td>K</td>
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<td>$\rho_b$</td>
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<tr>
<td>$\rho_g$</td>
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<td>$\mu$</td>
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<tr>
<td>$w_{\text{in},O_2}$</td>
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<td>$w_{\text{in},H_2O}$</td>
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<td>$w_{\text{in},CH_4}$</td>
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<tr>
<td>$w_{\text{in},CO_2}$</td>
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<tr>
<td>$w_{\text{in},H_2}$</td>
<td>0</td>
<td>[-]</td>
</tr>
</tbody>
</table>
Appendix-E: Definitions

- Bed porosity: \( \varepsilon_p = 0.38 + 0.073 \times \left( 1 + \left( \frac{D}{d_p} \right)^2 \right) \)

- Pellet porosity: \( \varepsilon_{cat} = 1 - \frac{\rho_b}{\rho_p} \)

- \( k_{dl} = \frac{150 \mu (1-\varepsilon_p)^2}{d_p^2 \varepsilon_p^3} \)

- \( k_{vi} = \frac{1.75 \rho_g (1-\varepsilon_p)}{d_p \varepsilon_p^3} \)

- \( \text{Sh} = \frac{\text{Convective mass transfer}}{\text{mass diffusion rate}} = \frac{K_g L}{D} \)

- \( k_{gi} = \left\{ \left( 0.765 N_{RE}^{-0.82} + 0.365 N_{Sc}^{-0.398} \right) / \varepsilon_p \right\} N_{RE} N_{Sc,j}^{1/3} \frac{D}{d_p} \)

- \( \text{Nu} = 2 + 1.1 \times (N_{Pr}^{0.33}) \times (N_{Re}^{0.6}) ; \)

- \( h = (0.91 \times N_{RE}^{-0.51} \times \psi) \frac{C_p \times m v}{N_{Pr}^{2/3}} \)

- \( \text{Conversion}, XA = \frac{\text{Molar flow of crude glycerol out}}{\text{Molar flow of crude glycerol in}} \times 100 \% \)

- \( \text{Yield} = \frac{\text{Molar flow of } H_2 \text{ out}}{\text{Molar flow of crude glycerol in}} \)

- \( \text{Effectiveness factor} = \frac{\text{Actual overall rate of reaction}}{\text{Rate of reaction with surface conditions}} = \frac{\text{Actual conversion rate}}{\text{Ideal conversion rate}} \)

Where the actual conversion rate = \( \int_0^r 4 \pi r^2 k C_A d r \)

- \( \text{Mach number} = \frac{\text{speed of object}}{\text{speed of light}} \)

Lower Mach number implies constant density
Appendix-F: Discretization

\[ \mathcal{E}_b \rho \left( \frac{1}{p} \frac{\partial p}{\partial t} \right) - \mathcal{E}_b \rho \left( \frac{1}{T} \frac{\partial T}{\partial t} \right) - \frac{\partial}{\partial z} \rho K \frac{\partial p}{\partial z} = 0 \]

Discretizing the above yields

\[
\left( \frac{\mathcal{E}_b^k \times \rho^k}{p^k \times \Delta t} \right) (p^k_{i+1} - p^k_i) - \left( \frac{\mathcal{E}_b^k \times \rho^k}{T^k_i \times \Delta t} \right) (T^k_{i+1} - T^k_i) - \\
\left( \frac{\rho^k_{i+1/2} \times K_p^k}{\Delta z} \right) \left( \frac{p^k_{i+1/2} - p^k_{i-1/2}}{\Delta z} \right) = 0
\]

Energy:

\[
\frac{(1-\mathcal{E}_b)}{\Delta t} C_p \rho_p + \mathcal{E}_b C_p, g \rho^k_i (T^k_{i+1} - T^k_i) + \frac{c_{p, g(i)} \rho^k_{i, z(i+1)} u^k_{i, z(i+1)}}{\Delta z} T^k_{i+1} - \\
\frac{c_{p, g(i-1)} \rho^k_{i, z(i-1)} u^k_{i, z(i-1)}}{\Delta z} T^k_{i-1} = \\
\frac{4U}{dt} (T_W - T') + S'
\]

Appendix-G: MATLAB code

1 D PH model
%%Geometry
function TransportAug25Feb10

% Effects of Axial Dispersion
L=0.045; % in m
nz=100;  dz=L/nz
z(1)=0;
z(2)=dz/2;
z(3:nz+1)=(z(2)+(1:nz-1)*dz);
z(nz+2)=z(nz+1)+dz/2;
zEdge(1:nz+1)=(0:nz)*dz;

% of catalyst pellet [J/KgK]
cpp=374.79 % 374 by Jason

% The number of species
ns=7;
% ns=[cG O2 N2 H2O H2 CH4 CO2]

% Constant for specific heat capacity [J/molK]
A(1:ns)=[9.656 29.526 29.342 33.933 25.399 34.942 27.437];
B(1:ns)=[4.283E-01 -8.99E-03 -3.54E-03 -8.42E-03 2.0178E-02 -3.99E-02 4.23E-02];
C(1:ns)=[-2.68E-04 3.81E-05 1.0076E-05 2.99E-05 -3.85E-05 1.92E-04 -1.96E-05];
D(1:ns)=[3.18E-08 -3.26E-08 -4.31E-09 -3.54E-09 -8.42E-09 2.0178E-08 -3.99E-09];
E(1:ns)=[2.77E-11 8.86E-12 2.59E-13 3.69E-12 -8.76E-12 3.93E-11 -2.99E-13];

% stoichiometric coefficient [-]
v(1:ns)=[1 0.65 0 0.7 3.2 0.5 2];

% standard heat of formation of species [kJ/mol]
Hf(1:ns)=[-582.8 0 0 -241.8 0 -74.85 -393.51];

% Standard heat of reaction [kJ/mol]
Hrnxo=(v(5)*Hf(5))+(v(6)*Hf(6))+(v(7)*Hf(7))-(v(1)*Hf(1))-(v(2)*Hf(2))-(v(3)*Hf(3))-(v(4)*Hf(4))

% diameter of pellets in m
dp=0.0008;

% Molecular weight of species Kg/kmol
M(1:ns)=[69 32 28 18 2 16 44];

% Boundary & Initial Conditions For Species
% Mole fraction of species [mol/mol]
yw(1) = 0.1;  yw(2) = 0.06; yw(3) = 0.23; yw(5) = 0.0000; yw(6) = 0.0000; yw(7) = 0.0000;
yw(4) = 1-(yw(1)+yw(2)+yw(3)+yw(5)+yw(6)+yw(7));
y(1:ns,1:nz)=0;
for is=1:ns
 y(is,1:nz)=yw(is);
end
y(3,1:nz)=yw(3);

% Average molecular weight of the mixture in Kg/kmol
Mavg=AvgMolarWt(y(1,:),y(2,:),y(3,:),y(4,:),y(5,:),y(6,:),y(7,:));
W(1:ns,1:nz)=0; WW(1:ns)=0;
%Mass fraction of species
for is=1:ns
    WW(is)=(M(is)*yw(is))/Mavg(1)
    W(is,1:nz)=WW(is)
end

%diameter of reactor in m
d=0.0127;
%universal gas constant in J/kmolK
R=8.314*1000;
Ru=8.314; %[J/molK]
%inlet temperature in K
Tambient=298;
Tw=773; %in K
T(1:nz)=Tw;
T0=Tambient;
% T0=500;

%density of pellet in kg/m3
Rop=8.77;%53.57;%8.77;
%effective thermal conductivity in W/mK where k(l) is at the edge
k2=0.062; %this if for i+1
k1=0.062; %this is for i-1
%heat transfer coefficent in W/m2K but U
h=550;

%Boundary & Initial Conditions For Flow and Heat
pW=1.05E5; %[in Pa]
pE=1.01325E5; %[Pa]
Press(1:nz)=pW;

%Concentration in [mol/m3]
ConcW=pW/(Ru*Tw)
Conc=(Press(1:nz))./(Ru.*T(1:nz));
ConcE=pW/(Ru*T(nz));

%Time
t=25;%TotalTime in s
dt=1E-4;
%Properties
%porosity
ep=0.38+0.073*(1+(((d/dp)-2)^2)/((d/dp)^2))

%viscosity in Pa.S
uv(1:nz)=0;
for il=1:nz
    [uv(il)]=viscosity(y(1:ns,il),T(il))
end

%density of gas mixture in kg/m3
Rog_in=(pW.*Mavg)/(R*Tw)
Rog(1:nz)=(Press.*Mavg)/(R*T)
RogE=((pE)*Mavg)./(R*(T(nz)))

%partial pressure calculations
P(is,1:nz)=0;
for is=1:ns
P(is,:)=y(is,:).*Press(:)'
end

%effectiveness factor for the rate
nk=0.98;

%Reaction order wrt crude glycerol[-]
m=1.06;

%Reaction order wrt water[-]

n=0.58;

%Reaction order wrt oxygen[-]
o=1.86;

%frequency factor units are [kmolC/kgcat.s.Pa^(m+n+o)]
Apr=((5.135*10^9)/(60*((101325)^(m+n+o))))
% % %Activation Energy[J/mol] this is because R is also in Kmols
An=-87800;

%Rate of reaction[molC/gcat.s] same as [kmolC/kgcat.s] to change to molC/kgcat.s
RR(1:nz)=(((Apr)*(exp(An./(Ru*(Tw))))).*((P(1,:)).^m).*((P(4,:)).^n).*
((P(2,:)).^o)))
RR0=RR(1,1);

% viscous pressure drop Units [kg/m4s]
kD(1:nz)=(150*uv(1:nz).*((1-ep)^2))/((dp^2)*(ep^3));%229188.56

%kinetic pressure drop [kg/m4]
KV=(1.75*Log(1:nz)*(1-ep))./dp*(ep^3) ;

% %inlet flowrate[mol/s]
FAO1=0.0019/60;
% FA(1:nz+1)=FAO1
% %Area
Area=(3.142*(d^2))/4;

vel(1:nz+1)=0.069012;

%The average velocity[m/s]
velAvg(1:nz)=(vel(1:nz)+vel(2:nz+1))/2;

%sum of viscous and kinetic term where kp(1) is at the edge-inverse
Kp(1:nz)=1./(kD+(kV.*velAvg(1:nz)));

%Initialize matrix for Press & Temp in density eqn
Ai(1:nz,1:2*nz)=0.0;
bp(1:nz)=0.0;

%for specific heat capacity of gas in J/kgK where cp(1) is at the edge
cpg(1:nz+1)=2020;
cP(1:ns,1:nz)=0;%units in [J/molK] and [J/KgK]
for is=1:ns
[cP(is,1:nz)]=SpHeat(nz,A(is),B(is),C(is),D(is),E(is),T);
end
% cpmolmix units J/molK
cPmolmix=(abs(((yw(7).*cP(7,:))+yw(6).*cP(6,:))+yw(5).*cP(5,:))- (yw(4).*cP(4,:))-yw(3).*cP(3,:))-yw(2).*cP(2,:))-yw(1).*cP(1,:));
\[
\text{cpg\_in} = ((\text{cPmolmix} \times 1000)) / \text{Mavg}; \text{units in J/KgK}
\]

\[
\text{cPmolmix} = \text{abs}(((y(7,:) \times \text{cP}(7,:)) + (y(6,:) \times \text{cP}(6,:)) + (y(5,:) \times \text{cP}(5,:)) - (y(4,:) \times \text{cP}(4,:)) - (y(3,:) \times \text{cP}(3,:)) - (y(2,:) \times \text{cP}(2,:)) - (y(1,:) \times \text{cP}(1,:))));
\]

\[
\text{cpg} = ((\text{cPmolmix} \times 1000)) / \text{Mavg}; \text{units in J/KgK}
\]

\[
\text{Hi}(1:nz) = 0; \text{(J/kmol)}
\]

for \( \text{ih} = 1:nz \)

\[
[\text{Hi}(\text{ih})] = \text{H\_rxn}(T(\text{ih}));
\]

end

\[
\% \text{Heat of reaction term[}
\]

\[
\text{Hrxn} = (((\text{Hrxno} \times 1E3) + ((\text{Hi}))) \times 1E3) / 2.5; \% \text{(Hrxno} \times 1E6) / 2.5 \text{ in J/Kmol C}
\]

\[
\% \text{Source term for temperature equation}
\]

\[
\text{SE}(1:nz) = (1-\text{ep}).*\text{(Rop)}.*((-1.\text{Hrxn})).*\text{nk}.*(\text{RR}));
\]

\[
\% \text{Diffusion coefficient}
\]

\[
\text{Dm}(1:ns) = [3.8E-5 1.03E-04 0 1.14E-04 3.64E-04 1.15E-04 7.94E-05];
\]

\[
\text{Dm}(1:ns) = [9.85E-5 6.881E-05 6.961E-05 8.544E-05 5.65E-04 7.467E-05 5.657E-05];
\]

for \( \text{is} = 1:ns \)

\[
\text{Deff}(\text{is},1:nz) = \text{Dm}(\text{is}).*\text{ones}(1,nz)
\]

end

\[
\% \text{Axial dispersion coefficient in m2/s}
\]

\[
\text{Dli}(\text{is},1:nz) = 0;
\]

for \( \text{is} = 1:ns \)

\[
\text{Dli}(\text{is},1:nz) = \text{Deff}(\text{is},1:nz);(0.73.*((\text{Dm}(\text{is}))) + (0.5*(\text{vel}(1:nz)))*\text{dp})./(1 + (9.49.*((\text{Dm}(\text{is}))) / ((\text{vel}(1:nz)))*\text{dp}));
\]

end

\[
\% \text{Source term for species equation}
\]

\[
\text{SW}(1,1:nz) = (((1-\text{ep}) \times \text{Rop}).*((\text{M}(1)))).*((\text{RR}(1:nz))).*((1 \times \text{v}(1))));
\]

\[
\text{SW}(2,1:nz) = (((1-\text{ep}) \times \text{Rop}).*((\text{M}(2)))).*((\text{RR}(1:nz))).*((1 \times \text{v}(2))));
\]

\[
\text{SW}(3,1:nz) = (((1-\text{ep}) \times \text{Rop}).*((\text{M}(3)))).*((\text{RR}(1:nz))).*((1 \times \text{v}(3))));
\]

\[
\text{SW}(4,1:nz) = (((1-\text{ep}) \times \text{Rop}).*((\text{M}(4)))).*((\text{RR}(1:nz))).*((1 \times \text{v}(4))));
\]

\[
\text{SW}(5,1:nz) = (((1-\text{ep}) \times \text{Rop}).*((\text{M}(5)))).*((\text{RR}(1:nz))).*((1 \times \text{v}(5))));
\]

\[
\text{SW}(6,1:nz) = (((1-\text{ep}) \times \text{Rop}).*((\text{M}(6)))).*((\text{RR}(1:nz))).*((1 \times \text{v}(6))));
\]

\[
\text{SW}(7,1:nz) = (((1-\text{ep}) \times \text{Rop}).*((\text{M}(7)))).*((\text{RR}(1:nz))).*((1 \times \text{v}(7))));
\]

\[
\% 1st term in temperature equation
\]

\[
a = (1-\text{ep}) \times \text{cpp} \times \text{Rop};
\]

\[
\text{Ap}(1:nz,1:nz) = 0.0;
\]

\[
\text{ApT}(1:nz,1:nz) = 0.0;
\]

\[
\text{AT}(1:nz,1:nz) = 0.0;
\]

\[
\text{bp}(1:nz) = 0.0;
\]

\[
\text{Ap}(1:nz,1:nz) = 0.0;
\]

\[
\text{ApT}(1:nz,1:nz) = 0.0;
\]

\[
\text{bT}(1:nz) = 0.0;
\]

\[
\text{bp}(1:nz) = 0.0;
\]

\[
\text{Aw1}(1:nz,1:nz) = 0.0;
\]

\[
\text{bW1}(1:nz) = 0.0;
\]

\[
\text{Aw2}(1:nz,1:nz) = 0.0;
\]

\[
\text{bW2}(1:nz) = 0.0;
\]

\[
\text{Aw4}(1:nz,1:nz) = 0.0;
\]

\[
\text{bW4}(1:nz) = 0.0;
\]

\[
\text{Aw5}(1:nz,1:nz) = 0.0;
\]
% %density update also found in the same script as Pressure
% for is=1:ns
% Dli(is,1:nz)=(0.73.*(Dm(is)))+((0.5*(vel(1:nz))*dp)./(1+(9.49.*(Dm(is))
)./((vel(1:nz)).*dp)));% end

% Breaking out the species calculations into their own *.m file
CalcSpecies;

% %viscosity in Pa.S
% uv(1:nz)=0;
for il=1:nz
[uv(il)]=viscosity(y(1:ns,il),T(il));
end

%velocity update
vel(1)=(-Kp(1))*(Press(1)-pW)/(0.5*dz);
vel(2:nz)=(-Kp(2:nz)).*(Press(2:nz)-Press(1:nz-1))./(dz);
vel(nz+1)=-((Kp(nz))*(pE-Press(nz))/(0.5*dz));

% The average velocity[m/s]
velAvg(1:nz)=(vel(1:nz)+vel(2:nz+1))/2;
velocity=vel(1:nz+1);

% viscous pressure drop Units [kg/m4s]
kD(1:nz)=(150*uv(1:nz).*((1-ep)^2))/((dp^2)*(ep^3));%229188.56

%kinetic pressure drop [kg/m4]
kV=(1.75*Rog(1:nz)*(1-ep))./dp*(ep^3) ;

%Kp update
Kp(1:nz)=1./(kD+(kV.*(velAvg(1:nz))));

% %for specific heat capacity of gas in J/kgK where cp(1) is at the
edge cp(g(1:nz+1)=2020;
cP(1:ns,1:nz)=0;%units in [J/molK] and [J/KgK]
for is=1:ns
[cP(is,1:nz)]=SpHeat(nz,A(is),B(is),C(is),D(is),E(is),T);
end
%cpmolmix units J/molK
cPmolmix=abs(((y(7,:).*cP(7,:))+(y(6,:).*cP(6,:))+(y(5,:).*cP(5,:)))+(y(4,:).*cP(4,:))+(y(3,:).*cP(3,:))+(y(2,:).*cP(2,:))+(y(1,:).*cP(1,:)));
cpg=((cPmolmix*1000)./Mavg);%units in J/KgK
%
for ipl=1:nz

[Hi(ipl)] = H_rxn(T(ipl));
end

%Hrnxn=((((Hrxns*1E3)+((Hi)))*1E3)/2.5;

%partial pressure calculations
P(is,1:nz)=0;
for is=1:ns
P(is,:) = y(is,:).*(Press(:)');
end

%Rate of reaction[molC/gcat.s] same as [kmolC/kgcat.s] to change to
%To find the actual rate in 0.25g of catalyst
RR(1:nz)=(((Apr)*(exp(An./(Ru*(T))))).*((P(1,:)).^m).*((P(4,:)).^n).*((P(2,:)).^o));
%%
RR(2:nz)=0;

RR0=RR(1,1);
Rxnrate=[RR0 RR(1:nz) RR(nz)];

%Source term for temperature equation
SE(1:nz)=(1-ep).*(Rop).*(((1-Hrxn)).*nk.*(RR));

%Source term update for species
SW(1,1:nz)=((1-ep)*Rop.*((M(1))).*((RR(1:nz)).*(-1*v(1))));
SW(2,1:nz)=((1-ep)*Rop.*((M(2))).*((RR(1:nz)).*(-1*v(2))));
SW(3,1:nz)=((1-ep)*Rop.*((M(3))).*((RR(1:nz)).*(-1*v(3))));
SW(4,1:nz)=((1-ep)*Rop.*((M(4))).*((RR(1:nz)).*(-1*v(4))));
SW(5,1:nz)=((1-ep)*Rop.*((M(5))).*((RR(1:nz)).*(-1*v(5))));
SW(6,1:nz)=((1-ep)*Rop.*((M(6))).*((RR(1:nz)).*(-1*v(6))));
SW(7,1:nz)=((1-ep)*Rop.*((M(7))).*((RR(1:nz)).*(-1*v(7))));

%Concentration update
ConcW=(pW/(Ru*Tw))/1000;
Conc1(1:nz)=(Press(1:nz)./(Ru.*T(1:nz)))/1000;
ConcE=(pW/(Ru*T(nz)))/1000;
Conc=[ConcW Conc1 Conc1(nz)]
figure (8)
if rem(it,0.005*nt)==0
plot(z',TempPlusBoundary), hold on
xlabel('reactor length (m)')
ylabel(' Temperature (K)')
end
end
hold off

figure (1)
plot(z,PressPlusBoundary)
assignin('base','PressPlusBoundary',PressPlusBoundary)
xlabel('reactor length (m)')
ylabel('Pressure (Pa)')
axis([0 0.045 1E5 1.06E5])

figure (2)
plot(zEdge',velocity)
assignin('base','velocity',velocity)
assignin('base','zEdge',zEdge)
xlabel('reactor length (m)')
ylabel('velocity (m/s)')
axis([0 0.045 0.0 inf])

figure (3)
plot(z',TempPlusBoundary)
assignin('base','TempPlusBoundary',TempPlusBoundary)
xlabel('reactor length (m)')
ylabel('Temperature(K)')
axis([0 0.045 773 inf])

figure (4)
plot(z',CG,''',z',O2,''',z',N2,''',z',H2O,''',z',H2,''',z',CH4,''',z',CO2,'')
assignin('base','SPE1',[CG,O2,N2,H2O,H2,CH4,CO2])
xlabel('reactor length (m)')
ylabel('mole fraction')
legend('CG','O2','N2','H2O','H2','CH4','CO2')
axis([0 0.045 0 1])

figure (5)
plot(z, XC)
assignin('base','XC',z)
assignin('base','XC',XC)
xlabel('reactor length (m)')
ylabel('conversion')
axis([0 0.045 0 inf])

figure (6)
plot(z,YH2)
assignin('base','YH2',YH2)
xlabel('reactor length (m)')
ylabel('Hydrogen yield')
axis([0 0.045 0 inf])

figure (7)
plot(z,Rxnrate)
assignin('base','Rxnrate',Rxnrate)
xlabel('reactor length (m)')
ylabel('reaction rate')
axis([0 0.045 0 inf])
end
function TransportJan22b

L=0.045; % in m
nz=100; dz=L/nz
z(1)=0;
z(2)=dz/2;
z(3:nz+1)=(z(2)+(1:nz-1)*dz);
z(nz+2)=z(nz+1)+dz/2;
zEdge(1:nz+1)=(0:nz)*dz;

% of catalyst pellet [J/KgK]
cpp=374.79 % 374 by Jason
% cpb=(1-ep)*cpp
%The number of species
ns=7;
%ns=[CG O2 N2 H2O H2 CH4 CO2]

% Constant for specific heat capacity [J/molK]
A(1:ns)=[9.656 29.526 29.342 33.933 25.399 34.942 27.437];
B(1:ns)=[4.283E-01 -8.99E-03 -3.54E-03 -8.42E-03 2.0178E-02 -3.996E-03 4.23E-02];
C(1:ns)=[-2.68E-04 3.81E-05 1.0076E-05 2.99E-05 -3.85E-05 1.92E-04 -1.96E-05];
D(1:ns)=[3.18E-08 -3.26E-08 -4.31E-09 -1.78E-08 3.19E-08 -1.53E-07 3.997E-09];
E(1:ns)=[2.77E-11 8.86E-12 2.59E-13 3.69E-12 -8.76E-12 3.93E-11 -2.99E-13];

% stoichiometric coefficient [-]
v(1:ns)=[1 0.65 0 0.7 3.2 0.5 2];

% standard heat of formation of species [kJ/mol]
Hf(1:ns)=[-582.8 0 0 -241.8 0 -74.85 -393.51];

% Standard heat of reaction [kJ/mol]
Hrxno=(v(5)*Hf(5))+(v(6)*Hf(6))+(v(7)*Hf(7))-(v(1)*Hf(1))-(v(2)*Hf(2))-(v(3)*Hf(3))-(v(4)*Hf(4));

% diameter of pellets in m % radius of pellet in m
dp=0.0008;
rp=dp/2;

%Molecular weight of species Kg/kmol
M(1:ns)=[69 32 28 18 2 16 44];

%Boundary & Initial Conditions For Species Mole fraction of
species [mol/mol]
yw(1) = 0.1;  yw(2) = 0.06;  yw(3) = 0.23;  yw(5) = 0.0000;  yw(6) = 0.0000;  yw(7) = 0.0000;
yw(4) = 1-(yw(1)+yw(2)+yw(3)+yw(5)+yw(6)+yw(7));
y(l:ns,1:nz)=0;
for is=1:ns
y(is,:)=yw(is)*ones(nz,1);
end
y(3,:) = yw(3)*ones(nz,1);

% Boundary & Initial Conditions For Species Mole fraction of species ON THE SOLID PHASE [mol/mol]
ywp(1) = 0.1; ywp(2) = 0.06; ywp(3) = 0.23; ywp(5) = 0.0000; ywp(6) = 0.0000; ywp(7) = 0.0000;
ywp(4) = 1-(ywp(1)+ywp(2)+ywp(3)+ywp(5)+ywp(6)+ywp(7));
yp(is,1:nz,1:nz)=0;
for is=1:ns
    yp(is,:) = ywp(is)*ones(nz,1);
end
yp(3,:) = ywp(3)*ones(nz,1);

% Average molecular weight of the mixture in Kg/kmol
Mavg = AvgMolarWt(y)

W(1:ns,1:nz)=0; WW(1:ns)=0;
% Mass fraction of species
for is=1:ns
    WW(is) = (M(is)*yw(is))/Mavg(1);
    W(is,1:nz)=WW(is);
end

% Mass fraction of species on catalyst surface
Wp(1:ns,1:nz)=W(1:ns,1:nz);

%diameter of reactor in m
d=0.0127;
% universal gas constant in J/kmolK
R=8.314*1000;
Ru=8.314; [%J/molK]
% inlet temperature in K
Tambient=298;
Tw=773; [% in K]
Tso=773; [% in K]
T=Tm*ones(1,nz);
Ts=Tso*ones(1,nz); [%K]
T0=Tambient;
% Tf=990;
%density of pellet in kg/m3
Rop=5.98;
% effective thermal conductivity in W/mK where k(1) is at the edge
k2=0.062; %this if for i+1
k1=0.062; %this is for i-1

% effective thermal conductivity in W/mK where k(1) for pellet
ks=0.348; %this if for i+1

% heat transfer coefficient in W/m2K but U
U=274;

% Boundary & Initial Conditions For Flow and Heat
pW=1.05E5; [% in Pa]
pE=1.01325E5; [%Pa]
\text{Press}=pW*\text{ones}(1,nz);

\% Concentration in [\text{mol/m}^3]
\text{ConcW}=pW/(Ru*Tw);
\text{Conc}=(\text{Press})./(Ru.*T);
\% Conc=(\text{Press}(1:nz))./(Ru.*T(1:nz));
\text{ConcE}=pW/(Ru*T(nz));

\% Time
\text{t}=25; \% TotalTime in s
\text{dt}=1E-3;
\text{nt}=15000;

\% Properties
\% porosity
\text{ep}=0.38+0.073*(1+(((d/dp)-2)^2)/((d/dp)^2));

\% Viscosity in Pa.S
\text{uv}(1:nz)=0;
\text{for } il=1:nz
\text{[uv(il)]=viscosity(y(1:ns,il),T(il));}
\text{end}

\% density of gas mixture in kg/m^3
\text{Rog}_\text{in}=(pW.*Mavg(1))/(R*Tw)
\text{Rog}(1:nz)=(\text{Press}.*Mavg)/(R*T)

\% Partial pressure calculations WRT BULK GAS PARTIAL PRESSURE
\text{P}(is,1:nz)=0;
\text{for } is=1:ns
\text{P}(is,:)=y(is,:).* (\text{Press});
\text{end}

\% Partial pressure calculations WRT solid phase PARTIAL PRESSURE
\text{PS}(is,1:nz)=0;
\text{for } is=1:ns
\text{PS}(is,:)=yp(is,:).* (\text{Press});
\text{end}

\% Molar density of mixture [\text{mol/m}^3]
\text{FA0}_m(1:ns,:)= (\text{P}(1:ns,:))/(Ru.*T);

\% Effectiveness factor for the rate
\text{nk}=0.98;
\% Reaction order wrt crude glycerol[-]
\text{m}=1.06;
\% Reaction order wrt water[-]
\text{n}=0.58;
\% Reaction order wrt oxygen[-]
\text{o}=1.86;
\% Frequency factor units are [kmol/C/kgcat.s.Pa^(m+n+o)]
\text{Aprr}=((15.135*10^9))/((101325)^{m+n+o})));
\% Activation Energy[J/mol] this is because R is also in Kmol
\text{An}=-87800;
% Rate of reaction [molC/gcat.s] same as [kmolC/kgcat.s] to change to molf/kgcat.s-wrt to the bulk gas 
RR=((((Apr)*(exp(An./(Ru*(Tw))))).*((P(1,:)).^m).*((P(4,:)).^n).*((P(2,:)).^o)))); 
RR0=RR(1,1);  

% Rate of reaction [molC/gcat.s] same as [kmolC/kgcat.s] to change to molf/kgcat.s-wrt to the bulk gas 
RRS=((((Apr)*(exp(An./(Ru*(Tso))))).*((PS(1,:)).^m).*((PS(4,:)).^n).*((PS(2,:)).^o))));  

% viscous pressure drop Units [kg/m4s] 
kD=(150*uv(1:nz).*((1-ep)^2))./(dp^2)*(ep^3));  

%kinetic pressure drop [kg/m4] 
kV=(1.75*Rog(1:nz)*(1-ep))./dp*(ep^3);  

% inlet flowrate[mol/s] 
FA01=0.0019/60;  

%Area 
Area=(3.142*(d^2))/4;  

%velocity  
vel(nz+1)=(-1*(pE-Press(nz)))/(kD(nz)*(0.5*dz)) 
velAvg(1:nz)=(vel(1:nz)+vel(2:nz+1))/2;  

%sum of viscous and kinetic term where kp(1) is at the edge-inverse 
Kp(1:nz)=1./(kD+(kV.*(velAvg(1:nz))));  

%Initialize matrix for Press & Temp in density eqn 
Ai(1:nz,1:2*nz)=0.0; 
bp(1:nz)=0.0;  

%for specific heat capacity of gas in J/kgK where cp(1) is at the edge 
cpg(1:nz+1)=2020;  
cP(1:ns,1:nz)=0;%units in [J/molK] and [J/KgK] 
for is=1:ns  
[cP(is,1:nz)]=SpHeat(nz,A(is),B(is),C(is),D(is),E(is),T); 
cpl(is,1:nz)=(((cP(is,1:nz))*1000)./(M(is))));  
end  

% cpmolmix units J/molK  
cPmolmix=abs(((yw(7).*cP(7,:))+(yw(6).*cP(6,:))+(yw(5).*cP(5,:)))-(yw(4).*cP(4,:))-(yw(3).*cP(3,:))-(yw(2).*cP(2,:))-(yw(1).*cP(1,:))));  
cpg_in=((cPmolmix*1000)./Mavg(1));%units in J/KgK  
cpg=(cpg_in(1))*ones(1,nz);%units in J/KgK  

%Diffusion coefficient  
Dm(1:ns)=[9.852E-5 6.881E-05 6.961E-05 8.544E-05 5.65E-04 7.467E-05 5.657E-05];
%Axial dispersion coefficient in m2/s
Dli(is, l: nz) = 0;
for is = 1: ns
Dli(is, l: nz) = (0.73.*(Dm(is)))/((0.5*(vel(l: nz))*dp)/(1+(9.49.*(Dm(is))\.
/(vel(l: nz).*dp))));
end

%velocity from mass flow velocity is the same as GS
mv(l: nz) = Rog(l: nz).*vel(l: nz);
uz = 0.069012; %mv./Rog

%Reynolds%!!!!!!!Heat transfer dimensionless parameters!!!!!!%%%%
NRe = (Rog.*dp.*vel(l: nz))./(uv(l: nz));
\%NRe = (Rog.*dp)./(uv(l: nz))%

%Friction factor for flow in porous media
fD = 6.8*((1-ep)^1.2)/(ep^3).*NRe.^-0.2;
\%https://www.quora.com/What-is-the-significance-of-the-Reynolds-number%

\%Prandtl number\%
NPr = (cpg.*uv).;/k1;

%Azial thermal conductivity%
k1f = (k1*(ep+((1-ep)/(0.139*ep)-0.0339+(2/3)*((0.05332^2)/13.8)))
\%effective thermal conductivity in W/mK where k(1) is at the edge
k11 = k1.*((k1f./k1)+(0.75.*NPr.*NRe));

\%Nusselt number\%
Nu = 2+1.1*(NPr.^0.333).*NRe.^0.6;

%Heat transfer coefficient
h = k1./(Nu.*dp);

NSc(l: ns, l: nz) = 0;
%Schmidts number
for is = 1: ns
NSc(is, l: nz) = ((uv(l: nz))./(Rog(l: nz)).*(Dm(is))))
Sh(is, l: nz) = k11*dp./(Dm(is))
end

\%Pellet calculation section \%
\%Volume
vpelette = 4/3*(pi)*((rp^3);
vreactor = (pi)*(((d^2/4)*L);
\%NUMBER OF CAtalyst=Total Volume of catalyst/volume of catalyst
Ncat = ((1-ep)*vreactor)/vpelette
area = 4*(pi)*((rp^2)
T_area = Ncat*area
av = (T_area/((1-ep)*vreactor)) %units in 1/m

Kgl(is, l: nz) = 0;
\%Mass transfer coefficientfor species
for is=1:ns
    Kgi1(is,1:nz)=(Dm(is))./(dp*(Sh(is,1:nz)))
end

%%%!!!!!!!!!!!!!!!Mass transfer dimensionless parameters!!!!!!!!!!

RHSKgi(1:nz)=((Kgi1(1,1:nz)).*av.*((Rog(1:nz)).*((Wp(1,1:nz))-
(W(1,1:nz))))+(Kgi1(2,1:nz)).*av.*((Rog(1:nz)).*((Wp(2,1:nz))-
(W(2,1:nz))))+(Kgi1(3,1:nz)).*av.*((Rog(1:nz)).*((Wp(3,1:nz))-
(W(3,1:nz))))+(Kgi1(4,1:nz)).*av.*((Rog(1:nz)).*((Wp(4,1:nz))-
(W(4,1:nz))))+(Kgi1(5,1:nz)).*av.*((Rog(1:nz)).*((Wp(5,1:nz))-
(W(5,1:nz))))+(Kgi1(6,1:nz)).*av.*((Rog(1:nz)).*((Wp(6,1:nz))-
(W(6,1:nz))))+(Kgi1(7,1:nz)).*av.*((Rog(1:nz)).*((Wp(7,1:nz))-
(W(7,1:nz))))
    assignin('base','RHSKgi',RHSKgi)

%Heat of reaction
Hi(1:nz)=0; % (J/kmol)
for ih=1:nz
    [Hi(ih)]=H_rxn(T(ih))
end

%Hrŕeat of reaction term
Hrxn=((((Hrxno*1E3)+((Hi)))*1E3)/2.5 in J/Kmol C

%Sourceterm for temperature equation for the bulk gas and solid phase respectively
SE(1:nz)=(1-ep).*(Rop).*((-1*Hrxn)).*nk.*(RR));
SEP(1:nz)=(1-ep).*(0.5).*((-1*Hrxn)).*nk.*(RRS));

% %Source term for species equation for bulk gas
SW(1,1:nz)=((1-ep)*Rop.*((M(1))).*((RR(1:nz)).*(-1*v(1))));
SW(2,1:nz)=((1-ep)*Rop.*((M(2))).*((RR(1:nz)).*(-1*v(2))));
SW(3,1:nz)=((1-ep)*Rop.*((M(3))).*((RR(1:nz)).*(-1*v(3))));
SW(4,1:nz)=((1-ep)*Rop.*((M(4))).*((RR(1:nz)).*(-1*v(4))));
SW(5,1:nz)=((1-ep)*Rop.*((M(5))).*((RR(1:nz)).*(1*v(5))));
SW(6,1:nz)=((1-ep)*Rop.*((M(6))).*((RR(1:nz)).*(1*v(6))));
SW(7,1:nz)=((1-ep)*Rop.*((M(7))).*((RR(1:nz)).*(1*v(7))));

% %Source term for species equation for solid phase
SWS(1,1:nz)=((1-ep)*Rop.*((M(1))).*((RRS(1:nz)).*(-1*v(1))));
SWS(2,1:nz)=((1-ep)*Rop.*((M(2))).*((RRS(1:nz)).*(-1*v(2))));
SWS(3,1:nz)=((1-ep)*Rop.*((M(3))).*((RRS(1:nz)).*(-1*v(3))));
SWS(4,1:nz)=((1-ep)*Rop.*((M(4))).*((RRS(1:nz)).*(-1*v(4))));
SWS(5,1:nz)=((1-ep)*Rop.*((M(5))).*((RRS(1:nz)).*(1*v(5))));
SWS(6,1:nz)=((1-ep)*Rop.*((M(6))).*((RRS(1:nz)).*(1*v(6))));
SWS(7,1:nz)=((1-ep)*Rop.*((M(7))).*((RRS(1:nz)).*(1*v(7))));

RHSKgii=SW(1,1:nz)+SW(2,1:nz)+SW(3,1:nz)+SW(4,1:nz)+SW(5,1:nz)+SW(6,1:nz)+SW(7,1:nz)
%
% 1st term in temperature equation
a=(1-ep)*cpp*Rop;
% Ts10=Tso+(((SE(1))-((h(1))*av*(Ts(1)-T(1))))*(dt))/(a)
Ap(l:nz,1:nz)=0.0;
ApT(1:nz,1:nz)=0.0;
AT(1:nz,1:nz)=0.0;
ATS(1:nz,1:nz)=0.0;
bT(1:nz)=0.0;
bTS(1:nz)=0.0;
bp(1:nz)=0.0;
Aw1(1:nz,1:nz)=0.0;
bW1(1:nz)=0.0;
Aw2(1:nz,1:nz)=0.0;
bW2(1:nz)=0.0;
Aw4(1:nz,1:nz)=0.0;
bW4(1:nz)=0.0;
Aw5(1:nz,1:nz)=0.0;
bW5(1:nz)=0.0;
Aw6(1:nz,1:nz)=0.0;
bW6(1:nz)=0.0;
Aw7(1:nz,1:nz)=0.0;
bW7(1:nz)=0.0;
y(is,1:nz)=0;

%!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!! Time Loop !!!!!!!!!!!!!!!!!!!!!!!!
nt =10000;
for it=1:nt

TempHET2217

% Temperature of pellet surface To find Temperature on catalyst
surface%
Tsl(1:nz)=0;
for i=1:nz
Tsl(i)=Ts(i)+(((SE(i))-((h(i))*av*(Ts(i)-T(i))))*(dt))/(a));
Tsl(nz-1)=Tsl(nz);
end
Tsl(1:nz)=Tsl(1:nz)
TSPlusBoundary=[Tso Ts(1:nz) Ts(nz)]

% Breaking out the species calculations into their own *.m file
SpeciesHET2911

% Breaking out the species calculations into their own *.m file
SpeciesHetJan22a

%Velocity
vel(1)=(-Kp(1))*(Press(1)-pW)/(0.5*dz)
for i=2:nz
vel(i)=(-Kp(i)).*(Press(i)-Press(i-1))./(dz);
end
vel(nz+1)=(-Kp(nz))*(pE-Press(nz))/(0.5*dz))

velocity=vel(1:nz+1)
% 
% velAvg(1:nz)=(vel(1:nz)+vel(2:nz+1))/2

% viscous pressure drop Units [kg/m4s]
kD=(150*uv(1:nz).*((1-ep)^2))/((dp^2)*(ep^3))\%229188.56

%kinetic pressure drop [kg/m4]
\[ \text{kV} = (1.75 \times \text{Rog} \times (1-\text{ep})) / \text{dp} \times (\text{ep}^3) \]
\[
\% \text{kV} = (1.75 \times \text{Rog}' \times (1-\text{ep})) / \text{dp} \times (\text{ep}^3) \\
\%
\]
\[
\% \text{Kp} \text{ update} \ \ \\
\text{Kp}(1:nz) = 1 / (\text{kD} + (\text{kV}(1:nz) \times \text{velAvg})) \\
\%
\]
\[
\% \text{Axial dispersion coefficient in m}^2/\text{s} \\
\text{Dli}(is,1:nz) = 0; \ \\
\text{for is}=1:ns \\
\text{Dli}(is,1:nz) = (0.73 \times (\text{Dm}(is))) \times ((0.5 \times (\text{vel}(1:nz) \times \text{dp}) / (1 + (9.49 \times (\text{Dm}(is)))) \times (\text{vel}(1:nz)) \times \text{dp})) \\
\text{end} \\
\%
\% \% \text{Molar density of mixture [mol/m}^3\% \\
\text{FA0}_\text{m}(1:ns,:) = (\text{P}(1:ns,:)) / (\text{Ru} \times \text{t}') \\
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% Mass transfer coefficient for species
for is=1:ns
    Kg11(is,1:nz)=(Dm(is))./(dp*(Sh(is,1:nz)))
end

% Heat of reaction
Hi(1:nz)=0;  % (J/kg mol)
for ih=1:nz
    [Hi(ih)]=H_rxn(T(ih))
end

% Heat of reaction term
Hrxn=((Hrxn0*1E3)+((Hi)))*1E3)/2.5 in J/kg mol C

% Partial pressure calculations
P(is,1:nz)=0;
for is=1:ns
    P(is,:)=y(is,:).*(Press(:)')
end

% Rate of reaction [mol C/kg cat.s] same as [kmol C/kg cat.s] to change to
mol C/kg cat.s
RR(1:nz)=((((Apr)*(exp(An./(Ru*(T'))))).*((P(1,:)).^m).*((P(4,:)).^n).*
          ((P(2,:)).^o)))
Rxnrate=[RR0 RR(1:nz) RR(nz)]

% Source term for temperature equation
SE(1:nz)=(1-ep).*(Rop).*(((-1*Hrxn)).*nk.*(RR))
% Source term for species equation
SW(1,1:nz)=((1-ep)*Rop.*((M(1))).*((RR(1:nz)).*(-1*v(1))))
    +(1-ep)*Rop.*((M(2))).*((RR(1:nz)).*(-1*v(2))))
SW(3,1:nz)=((1-ep)*Rop.*((M(3))).*((RR(1:nz)).*(-1*v(3))))
    +(1-ep)*Rop.*((M(4))).*((RR(1:nz)).*(-1*v(4))))
SW(5,1:nz)=((1-ep)*Rop.*((M(5))).*((RR(1:nz)).*(1*v(5))))
SW(6,1:nz)=((1-ep)*Rop.*((M(6))).*((RR(1:nz)).*(1*v(6))))
SW(7,1:nz)=((1-ep)*Rop.*((M(7))).*((RR(1:nz)).*(1*v(7))))

RHSKgii=SW(1,1:nz)+SW(2,1:nz)+SW(3,1:nz)+SW(4,1:nz)+SW(5,1:nz)+SW(6,1:nz)+SW(7,1:nz)

% Concentration update
ConcW=(pW/(Ru*Tw))/1000
Conc1(1:nz)=(Press(1:nz)./(Ru.*T(1:nz)))/1000
ConcE=(pW/(Ru*T(nz)))/1000
Conc=[ConcW Conc1 Conc1(nz)]

figure (10)
if rem(it,0.005*nt)==0
    plot(z',TempPlusBoundary), hold on
    xlabel('reactor length (m)')
    ylabel(' Temperature (K)')
end
end
hold off

figure (1)
plot(z, PressPlusBoundary)
assignin('base', 'PressPlusBoundary', PressPlusBoundary)
xlabel('reactor length (m)')
ylabel('Pressure (Pa)')
axis([0 0.045 1E5 1.06E5])

figure (2)
pplot(zEdge', velocity)
assignin('base', 'velocity', velocity)
assignin('base', 'zEdge', zEdge)
xlabel('reactor length (m)')
ylabel('velocity (m/s)')
axis([0 0.045 0 1])

figure (3)
pplot(z, TempPlusBoundary)
assignin('base', 'TempPlusBoundary', TempPlusBoundary)
xlabel('reactor length (m)')
ylabel('Temperature (K)')
axis([0 0.045 773 0])

figure (4)
pplot(z, TSPlusBoundary)
assignin('base', 'TSPlusBoundary', TSPlusBoundary)
xlabel('reactor length (m)')
ylabel('Temperature of pellet (K)')
axis([0 0.045 773 0])

figure (5)
pplot(z, CG, 'O2', 'N2', 'H2O', 'H2', 'CH4', 'CO2')
assignin('base', 'SPE', [CG, O2, N2, H2O, H2, CH4, CO2])
xlabel('reactor length (m)')
ylabel('mole fraction')
legend('CG', 'O2', 'N2', 'H2O', 'H2', 'CH4', 'CO2')
axis([0 0.045 0 1])

figure (6)
pplot(z, CGS, 'O2S', 'N2S', 'H2OS', 'H2S', 'CH4S', 'CO2S')
assignin('base', 'SPE1', [CGS, O2S, N2S, H2OS, H2S, CH4S, CO2S])
xlabel('reactor length (m)')
ylabel('mole fraction')
legend('CGS', 'O2S', 'N2S', 'H2OS', 'H2S', 'CH4S', 'CO2S')
axis([0 0.045 0 1])

figure (7)
pplot(z, XC)
assignin('base', 'z', z)
assignin('base', 'XC', XC)
xlabel('reactor length (m)')
ylabel('conversion')
axis([0 0.045 0 1])

figure (8)
plot(z,YH2)
assignin('base','YH2',YH2)
xlabel('reactor length (m)')
ylabel('Hydrogen yield')
axis([0 0.045 0 inf])

figure (9)
plot(z,Rxnrate)
assignin('base','Rxnrate',Rxnrate)
xlabel('reactor length (m)')
ylabel('reaction rate')
axis([0 0.045 0 inf])
end
Appendix H: Concept of Reaction

The steps required for the reaction to proceed is given below

1. External mass transfer also known as diffusion where the reactants diffuse from the bulk fluid to surface of the catalyst by virtue of a driving force.

2. Internal mass transfer: This is the reverse of external mass transfer. The reactants travel from the external surface of the catalyst to the active sites located inside the pellet.

3. Adsorption of reactants on active sites

4. Surface reaction

5. Desorption of products

6. Diffusion of products from active sites to external surface

7. Mass transfer of products from pellet surface to bulk fluid