Kinetic Analysis of the Existing Models of Methanol Steam Reforming for Hydrogen Production

By

Kamarulzaman Bin Nasib
8121

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JAN 2010

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Kinetic Analysis of the Existing Models of Methanol Steam Reforming for Hydrogen Production

By

Kamarulzaman Bin Nasib

8121

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

Approved by,

(AP Dr Ye Lwin)
Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
JAN 2010

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

KAMARULZAMAN BIN NASIB

ACKNOWLEDGEMENTS

السلا م عليكم ورحمة ألله وبركاته
بسم ألله الرحمن الرحيم

Firstly, I would like to thank Allah the Almighty for His willing and blessing so that I successfully finished my dissertation. Secondly, I would like to thank Universiti Teknologi PETRONAS for providing me such a good environment and facilities like internet services, Information Resource Center and many more.

I would also like to thank my supervisor, A.P Dr Ye Lwin who has helped me a lot during the whole period in completing this project. Without his helps and advices, I would not have done the project well.

Last but not least, thanks to our entire colleague in giving me positive feedback, supportive, co-operation while completing this report.
Thank you.

Yours Sincerely,
Kamarulzaman Bin Nasib

ABSTRACT

Steam Reforming of Methanol (SRM) reaction has been highly developed and thoroughly studied process. Liwei Pan (2005) stated that it can offer the highest maximum hydrogen content in the product gas (75%) while maintaining a high selectivity towards the harmful product carbon dioxide. SRM thus now becomes the world's new potential technique of producing hydrogen gas by reacting methanol and steam at certain optimum temperature. Hydrogen gas is now becoming an increasingly important source of fuel for today which is widely used for the Proton Exchange Membrane Fuel Cells (PEMFC) and it also used by various industrial processes. As a result, many researchers have been seriously studying the kinetics of the SRM in order to investigate the nature of the process and then develop the best way to produce hydrogen gas through steam reforming technique. This research will attempt to study the two widely accepted kinetic models of SRM proposed by two authors; Peppley and Patel & Pant. Both of the authors have proposed two different models pertaining to the mechanism of the SRM. Since the models are already available, comparison will be made by taking both models into simulation mode. The Microsoft Excel software will be used to simulate kinetic models and the concentration profile as well as the kinetic rate profile will be compared.

In this report, the literature reviews of the various journals are made pertaining to the steam reforming of methanol in the study of hydrogen production. Matters such as the reaction path proposed by different authors, the discussion about the newly developed proton exchanged membrane fuel cell (PEMFC), thermodynamics consistency, carbon monoxide (CO) formation associated to the steam reforming of methanol and also the preventive action to minimize CO formation is discussed in detail in the report. Besides that, the expected results are also shown which are obtained by different authors through experimental and simulation work.

It is learned from the result of the simulation that the Peppley Model is better if compared to the Patel-Pant Model. The Peppley Model seems to be more robust. It is because the model is consistent with the local thermodynamic. The Patel-Pant Model has got inconsistency in it, though it shows some better characteristics compared to the one of Peppey such as in the flowrate profile as well as in the least production of the carbon monoxide gas, CO. However, the Peppley model needs to be modified to make it a better model. The rate expression need to be further simplified as the one proposed by Purnama *et. al* (2004). Last but not least, the WGS reaction rate expression must be changed so that it can suit the RWGS trend that is actually happening in the Peppley Model.

TABLE OF CONTENT

CHAPTER 4: RESULT EVALUATION

CHAPTER 1: INTRODUCTION

1.1 BACKGROUND OF STUDY

Hydrogen is generally expected to play an important role in the future energy systems. Hydrogen is regarded as a primary energy carrier in the future by virtue of the fact that it can be produced from renewable sources such as biomass, solar energy, and so on, and it is efficiently converted to electricity by fuel cells. In recent years, much attention has been paid to the use of hydrogen as an energy carrier in fuel cells and mobile vehicles, due to its high-efficiency and very low to zero pollution (Liwei Pan, 2005). Hydrogen can be produced on-board of fuel-cell-powered vehicles by steam reforming of liquid fuels such as methanol, ethanol, gasoline and diesel, which have high-energy storage density (Purnama *et al.*, 2004).

Polymer electrolyte fuel cells (PEMFCs) have presently attracted much attention worldwide since it provides high efficiency with clean exhaust gas by consuming hydrogen and oxygen. Development of hydrogen production has been widely studied to commercialize the production process. Reforming of fuels, such as, methanol, ethanol, gasoline, biogas, natural gas and dimethyl ether has been developed. For hydrogen production, steam reforming (SR), partial oxidation (PO), and auto thermal steam reforming (ATR) are the major processes for reforming of those fuels. PO and ATR processes have a merit on fast start-up time because of exothermic nature of oxidation reaction (Kajornsak, 2006). However, the PO and ATR processes provide lower efficiency and reformate quality, i.e., lower hydrogen production yield, higher rate of side reactions, and by-products. SR process gives high concentration of hydrogen at about 70–80% on a dry basis, while those for PO and ATR are estimated to be ca. 40–50% on a dry basis. Methanol appears to be a suitable liquid fuel for on-board hydrogen production.

Steam reforming of methanol has widely been developed. Generally, it can be operated at low temperature of 250–300 °C. Natural gas and biogas can be reformed at relatively high temperature of 600–800 °C. These fuels normally contain sulfur compounds that can poison reforming catalysts. Thus, a desulfurizer unit is needed for the reforming system. From the technological point of view, methanol clearly has distinct advantages as a hydrogen-carrier for the sake of fuel cell vehicle applications. Methanol is liquid at atmospheric conditions and has a high hydrogen-to-carbon ratio compared to other candidates. Since methanol has a high H/C ratio and no C–C bonds, this will minimizes the risk for coke formation to happen.

Moreover, as methanol can be produced from renewable sources, its reforming does not contribute to a net addition of CO_2 to the atmosphere. Furthermore, methanol can be reformed to hydrogen at much lower temperatures (200–300 °C), and is more efficient as compared to gasoline which requires high temperature (700–800 °C). In addition, methanol is an environmentally friendly fuel, as it is readily biodegradable in air, soil and water. When methanol is used in a fuel cell vehicle, emissions are extremely low.

Mechanisms for methanol-steam reforming on $Cu/ZnO/Al_2O_3$ catalysts are developed which account for all three of the possible overall reactions: methanol and steam reacting directly to form H_2 and CO_2, methanol decomposition to H_2 and CO and the water-gas shift reaction (Peppley, 1998).

The major products of steam reforming of methanol were hydrogen and carbon dioxide with small amount of carbon monoxide which is formed as a secondary product (Patel, Pant, 2007). Methanol, as a reactant in steam reformation, is a relatively inexpensive renewable fuel that produces less environmentally harmful products than the internal combustion of conventional petroleum fuel (Kearns, et al, 2009). Among all possible choices of fuels, methanol is considered to be the most favorable candidate due to its high ratio of hydrogen to carbon and low reaction temperatures (Cao, et al, 2006).

1.2 PROBLEM STATEMENT

Recently, the possibility of using an on-board methanol-steam reformer to generate hydrogen for a fuel cell engine in various transportation applications has resulted in an increased interest in the study of the methanol-steam reforming process. However, at the operating temperature of PEMFC, the electro catalyst at the anode is extremely sensitive to CO poisoning. For this reason it is highly desirable to validate the existing kinetic models by including the estimation of CO formation.

This is very significant research because if the best model in the production of hydrogen can be proven theoretically as well as experimentally, the manufacturer will have a better understanding to produce hydrogen in their PEMFC with as safer and lower cost as possible. In this research, the aim is to evaluate the existing kinetic model that can give the best rate of production of the main desired product, which is the hydrogen gas and model that can minimize the side product carbon monoxide as well as carbon dioxide.

1.3 OBJECTIVES

The objectives of the current project are:

- To check for thermodynamic consistency of the kinetic models used in the steam reforming of methanol.
- To see the possible differences in the concentration and rate profiles of the two most widely accepted kinetic models of methanol steam reforming.
- To propose a kinetic model that is thermodynamically consistent and represents a minimum number of reactions involving the primary components of the reaction mixture.

1.4 SCOPE OF STUDY

The project is divided into three different phases in order to achieve its golden objectives. The first phase covers the literature review part. This phase is very much important in order to get the first insight and understanding of the topic of the research. Thus coverage on background of study, the study of the mechanism of the kinetic models is being made.

During the second phase of the project, the objectives of the research should now be stated to ensure that student will focus into the requirement of the project. Methodology of the project is also determined in this phase which guides the student the step by step method in addressing the problem. Still under this phase, the implementation strategy is identified.

The student is required to use the Microsoft Excel Software for the purpose of simulation. The reason to have the simulations for the both models are is to observe the different characteristics shown by the two models proposed by Peppley and Patel& Pant. The final phase of the project will be the evaluation and presentation of the results achieved during the simulation.

In this research, only the steady state simulation of the pseudo-homogenous plug-flow model is being considered. Hence, only the ordinary differential equation in one dimension is involved. In addition, it is assumed that the isothermal condition is made so that energy balance is not considered and only the continuity equation is involved.

CHAPTER 2: LITERATURE REVIEW AND THEORY

2.1 METHANOL STEAM REFORMING

Literature review has been made to see the various research and finding of the different authors in the field of methanol-steam reforming (SRM). As to be more focus to the kinetic model involving the methanol steam reforming reaction, Peppley model and Patel-Pant model of the kinetic analysis were chosen as the main references in this research.

The kinetic model presented by the Peppley is based on the three possible overall reactions; methanol and steam reacting directly to form H_2 and CO_2, methanol decomposition to H_2 and CO and the water-gas shift reaction (Peppley, et al. 1999). Those three reactions are shown as follow;

1. Steam Reforming Methanol (SRM)
   $CH_3OH + H_2O \leftrightarrow 3H_2, \quad \Delta H^{\circ} = 49kJ\,mol^{-1}$
2. Methanol Decomposition (MD)
   $CH_3OH \leftrightarrow 2H_2 + CO, \quad \Delta H^{\circ} = 91kJ\,mol^{-1}$
3. Water Gas Shift (WGS)
   $CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H^{\circ} = -41kJ\,mol^{-1}$

The kinetic model proposed by the author is based on the analysis in surface mechanism. They are several key features of the mechanism presented by Peppley. Firstly, hydrogen adsorption does not compete for the active sites with the oxygen-containing species. Secondly there are separate active sites for the decomposition reaction distinct from the active sites for the methanol-steam reaction and the water-gas shift reaction. Thirdly, rate-determining step (RDS) for both the methanol-steam reaction and the methanol decomposition reaction is the dehydrogenation of adsorbed methoxy groups and (IV) the RDS for the water-gas shift reaction is the formation of an intermediate formate species.

The Patel-Pant Model is based on the direct reaction between methanol and the steam to produce H_2 and CO_2 and the reverse of the water-gas shift reaction (RWGS). The reactions are shown below;

1. Steam Reforming Methanol (SRM)

   $$CH_3OH + H_2O \leftrightarrow 3H_2, \quad \Delta H^{\circ} = 49 kJ\, mol^{-1}$$

2. reverse of the water-gas shift reaction (rWGS)

   $$CO_2 + H_2 \leftrightarrow CO + H_2O, \Delta H^{\circ} = 41\, kJ\, mol^{-1}$$

These reactions take place on the Cu/ZnO/Al2O3 catalyst which has led to the development of mechanistic kinetic model using Langmuir–Hinshelwood (LH). The kinetics study was performed over a wide range of reaction temperature and contact-time in an integral reactor under the conditions of no diffusion limitation. These two different mechanisms lead to different kinetic rate expressions. Simulation is required to see the similarity and the differences that exist between the two models

Lee (2004) in his study proposed that the reaction sequence of the steam reforming is methanol decomposition followed by WGS reaction. He stated that the decomposition step was the rate-determining for the whole process.

$CH_3OH \rightarrow CO + 2H_2$

$CO + H_2O \leftrightarrow CO_2 + H_2$

Since CO is being produced in the reaction sequence, the CO concentration in the products should at least be equal to or greater than the concentration of the WGS equilibrium. However this is not well-supported in the experiments of the studies that proposed the reaction sequence. However in the latest studies, (Lee, 2004) it was discovered that the reaction between methanol and water occurs directly to produce carbon dioxide and hydrogen.

$$2CH_3OH \rightarrow CH_3OCHO + 2H_2$$
$$CH_3OCHO + H_2O \rightarrow CH_3OH + HCOOH$$
$$HCOOH \rightarrow CO_2 + H_2$$

A methyl formate reaction route has been suggested for the reaction as shown above. Jiang (1993) claimed in his research that CO is not the primary product and it does not involve in the expression.But he said that the CO is highly produced by the rWGS reaction which uses the product of the reforming reaction as shown below;

$$CO_2 + H_2 \rightarrow CO + H_2O$$

There are some notable differences in the proposed reaction mechanisms are in the assumption on the active sites for the adsorbed species as for Lee and Peppley. Lee (2004) assumed that all adsorbed species compete on a single kind of active sites on the surface of the catalyst, whereas Peppley et al. assumed two distinct types of active sites, one type exclusively for hydrogen adsorption and the other type for all other adsorbed species. Although, the elementary reactions and the rate-determining step (RDS) in the mechanisms are the same, the resulting rate expressions will differ in their predictions for a reaction mixture which is absent of hydrogen.

2.2 PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC)

In the world today, there is an increasing interest in methanol as a fuel for power units based on its low-temperature small size fuel cells, mainly of the PEMFC type (Arzamendi, et al, 2008). It is reported that strong efforts are being made to commercialize the use of PEMFC for the generation of electric power for both electric vehicles and electric power plants (Birdsell and Vandcrborgh, 1994; Vandcrborgh *et al.*, 1987; Dunnison and Wilson, 1994). Fuel cell energy systems have attracted much attention due to their high energy efficiencies and power densities (Dagle ,Wang,Chin, 2009).

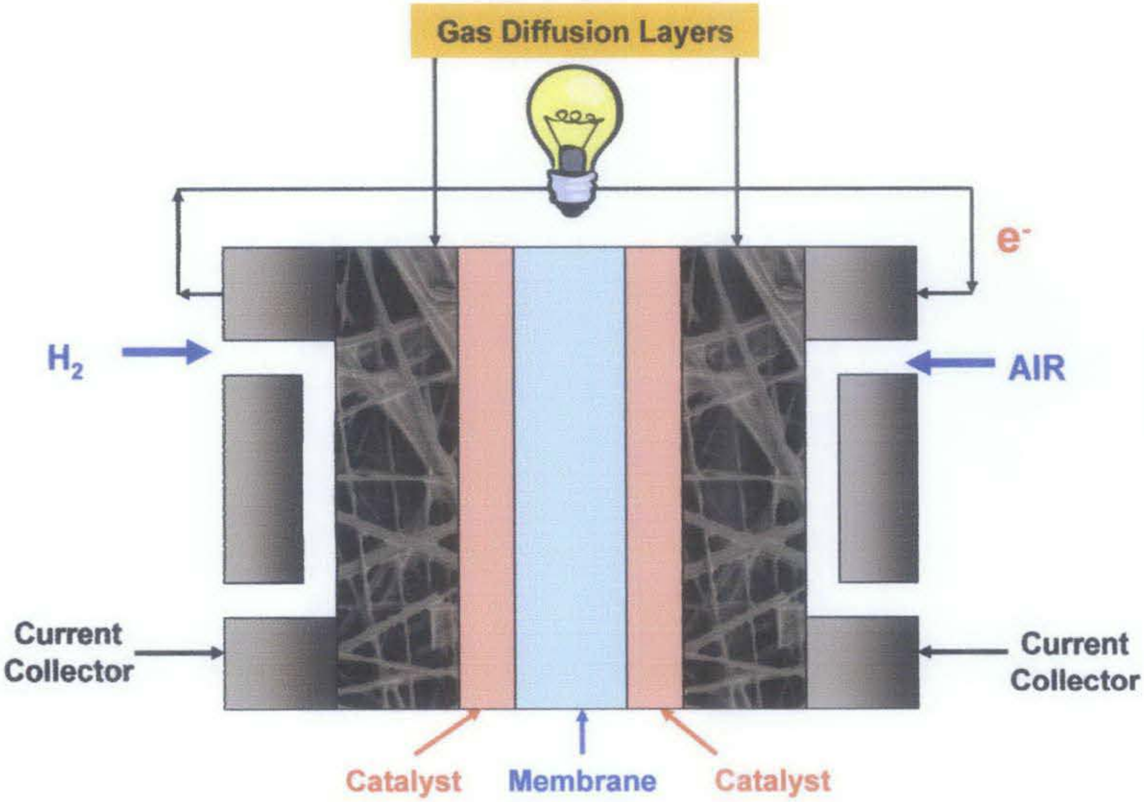

Figure 1: schematic diagram of proton exchange membrane fuel cell (PEMFC)

Unlike internal combustion engines (ICEs), fuel cells are not limited by the thermal efficiency of the Carnot cycle. Hence, the fuel utilization is much more efficient than in conventional heat engines. Furthermore, fuel cells are silent during operation and have no moving parts, and the emissions of hazardous compounds to the atmosphere are low or even non-existing. Current trends indicate that PEMFC vehicles will use liquid fuels, at least in the early stages of commercialization. Methanol is a fuel, which is readily available and can be catalytically converted into a H_2-rich gas at moderate temperature (200–300 ◦C).

2.3 THERMODYNAMICS CONSISTENCY

Rate equation and their coefficient in network are not entirely independent (Helfferich, 2004) . They are subject to two constraints: those of thermodynamics consistency and also the so-called microscopic reversibility. For reversible reaction such as the water gas shift reaction (WGS), the algebraic form of the rate equation of the forward reaction imposes a constraint on that of the rate equation of the reverse reaction. Thermodynamics consistency and microscopic reversibility can be used to verify that the postulated values of the coefficients constitute a self-consistent set or to obtain a still missing coefficient value from those of the others.

At equilibrium for any reversible reaction, there is no net formation or no net consumption of reactants and products respectively, that is, the forward and reverse reaction rates must equal (Helfferich, 2004). This is true no matter how many steps reactions are involves. Thus it is said that "equating forward and reverse rates must lead to an expression that is compatible with the mass-action law of equilibrium".

The fact can be used as a self-consistency check of postulated equations for the forward and reverse rates and their coefficients; or as a help in deriving the reverse rate equation from the forward one; or to calculate the reverse rate coefficient from the forward one and the equilibrium constant, or the forward rate coefficient from the reverse one and the equilibrium constant.

To see how the thermodynamics consistency criterion can help in the search for a reverse rate equation compatible with the empirical forward equation, let's consider the example below:

Stoichiometry: $2A \longleftrightarrow P$
Equilibrium requirement: Cp/C_A^2 =constant = K_{AP}
Empirical forward rate: $\overrightarrow{r_p} = K_a C_A^{1.35}$
A likely reverse rate equation is reverse rate: $-\overleftarrow{r_p} = k_b C_p/C_A^{0.65}$
It is compatible because equating the forward and reverse rates gives the following equation which is in accordance with the equilibrium requirement.

K_a/k_b = constant = $C_p/C_A^{1.35}C_A^{0.65} = C_p/C_A^2 = K_{AP}$

However the reverse rate equation is not unique. But any equation with constant n chosen at will meets the equilibrium requirement. This is shown below;
Reverse rate: $-r_p^{\,n} = k_b^{\,n} C_p^{\,n}/C_A^{2n-1.35}$
When K_a/K_b = constant = $C_p^{\,n}/C_A^{2n-1.35+1.35} = C_p^{\,n}/C_A^{2n} = (C_p/C_A^{2})^{n} = K^n_{AP}$
So if K^n_{AP} is a contant so is K_{AP}

Forward and reverse reaction must also occur along the same pathway (Helfferich, 2004). The reverse reaction is not allowed to take a different path even it is partially. This is because that would create a loop with net circular reaction. This will also apply to catalytic reaction.

2.4 CO FORMATIONS AS DRAWBACK

One of the main drawbacks of methanol–steam reforming is the formation of CO as a by-product to the major products hydrogen and carbon dioxide. As reported in the literature (Agrell, 2001) CO levels can be influenced by the temperature of the reactor, degree of conversion of the methanol, molar ratio of methanol and water, and addition of oxygen to the methanol–steam mixture. The experimental results of CO partial pressure as a function of contact time at different reaction temperatures show very clearly that CO was formed as a consecutive product (Purnama *et al.*, 2004).

CO produced in the steam reforming reaction is currently a poison to the promising PEMFC and as a result much attention has been focused on the mechanism of CO formation during the reaction. In comparison to other impurities such as CH_4, HCHO, and HCOOH, the poisoning effect of CO was found to have the largest influence on the fuel cell performance. The product gas, thus needs further purification, i.e. the removal of CO, to be used in PEMFC, since the anode catalyst of the fuel cell is poisoned by CO with a concentration as low as 10 ppm.

2.5 STRATEGIES TO PREVENT CO FORMATION

The results of the kinetic studies, however, showed that CO did not form when methanol was present and that CO_2 and H_2 were the primary products, but that when methanol was fully converted, CO was evident in the gas stream (John, 1999). Purnama et al (2004) however suggested that there are three possibilities to prevent CO from being introduced into the fuel cell:

(i) an extra module is added between the steam reforming reactor and the fuel cell (CO clean-up unit), such as separation of hydrogen using Pd membranes or the selective oxidation of CO

(ii) a new design for the reformer reactor is employed, i.e. purification integrated in the reformer reactor, or

(iii) a new catalyst is developed that is active for steam reforming, but does not produce CO.

Lee et al (2004) suggested that the preferential oxidation of CO (PROX) with oxygen can be used to remove CO in hydrogen. In this respect, the production of hydrogen with methanol for PEM fuel cells consists of two reaction stages: steam reforming and PROX.

CHAPTER 3: METHODOLOGY / PROJECT WORK

3.1 LITERATURE OF THE MODEL

This project is designed to be completed in three main phases which are literature review of the models, project simulation and results evaluation. Project research is done by making references to different kinetics models journal of steam reforming of methanol based on various mechanism proposed by different authors. In this project, the Peppley Model and Patel-Pant Model are chosen to be compared.

3.2 PROJECT SIMULATION

There will be a simulation required to learn the behaviors of the chosen kinetics models in terms of their concentration profile, kinetic rate profile, etc. Microsof EXCEL software will be used in this simulation.

The models considered are those proposed by Peppley *et al.* (1999) and Patel & Pant (2007). The Peppley model is based on the reforming-decomposition-water-gas shift (WGS) mechanism. It consists of rate expressions in Langmuir-Hinshelwood (L-H) form for reforming, decomposition, and WGS reaction. The reactions are as explain below;

1. A hydrogen-rich gas can be produced by steam reforming of methanol (SRM) over a copper-based catalyst at temperatures of 200-300°C:

$$CH_3OH(g) + H_2O(g) \rightarrow CO_2(g) + 3H_2(g) \qquad \Delta H^0_{298} = 49.4 \text{ kJ/mol} \tag{1}$$

2. In addition, Peppley *et al.* (1999) have proposed that the CO can be produced at low methanol conversion i.e. at low residence time, by the decomposition of methanol:

$$CH_3OH(g) \rightarrow CO(g) + 2H_2(g) \qquad \Delta H^0_{298} = 91.0 \text{ kJ/mol} \tag{2}$$

3. However, the Steam Reforming Process produces CO as a by-product, evidently by the reversible water-gas shift (RWGS) reaction at high methanol conversions (Agrell, *et al.*, 2001; Patel and Pant, 2007; Purnama *et al.*, 2004):

$$CO_2\,(g) + H_2\,(g) \leftrightarrow CO\,(g) + H_2O\,(g) \qquad \Delta H^0_{298} = 41.2 \text{ kJ/mol} \tag{3}$$

3.2.1 RATE OF EXPRESSION

Methanol–steam reaction:

$$r_R = \frac{k_R K^*_{CH_3O^{(1)}}\left(p_{CH_3OH}/p_{H_2}^{1/2}\right)\left(1 - p_{H_2}^3 p_{CO_2}/k_R p_{CH_3OH} p_{H_2O}\right) C^T_{S_1} C^T_{S_{1a}}}{\left(1 + K^*_{CH_3O^{(1)}}\left(p_{CH_3OH}/p_{H_2}^{1/2}\right) + K^*_{HCOO^{(1)}} p_{CO_2} p_{H_2}^{1/2} + K^*_{OH^{(1)}}\left(p_{H_2O}/p_{H_2}^{1/2}\right)\right)\left(1 + K^{1/2}_{H^{(1a)}} p_{H_2}^{1/2}\right)}.$$

Water-gas shift reaction:

$$r_W = \frac{k^*_W K^*_{OH^{(1)}}\left(p_{CO} p_{H_2O}/p_{H_2}^{1/2}\right)\left(1 - p_{H_2} p_{CO_2}/k_W p_{CO} p_{H_2O}\right) C^{T^2}_{S_1}}{\left(1 + K^*_{CH_3O^{(1)}}\left(p_{CH_3OH}/p_{H_2}^{1/2}\right) + K^*_{HCOO^{(1)}} p_{CO_2} p_{H_2}^{1/2} + K^*_{OH^{(1)}}\left(p_{H_2O}/p_{H_2}^{1/2}\right)\right)^2}.$$

Decomposition reaction:

$$r_D = \frac{k_D K^*_{CH_3O^{(2)}}\left(p_{CH_3OH}/p_{H_2}^{1/2}\right)\left(1 - p_{H_2}^2 p_{CO}/k_D p_{CH_3OH}\right) C^T_{S_2} C^T_{S_{2a}}}{\left(1 + K^*_{CH_3O^{(2)}}\left(p_{CH_3OH}/p_{H_2}^{1/2}\right) + K^*_{OH^{(2)}}\left(p_{H_2O}/p_{H_2}^{1/2}\right)\right)\left(1 + K^{1/2}_{H^{(2a)}} p_{H_2}^{1/2}\right)}.$$

To represent the reforming-reverse WGS (RWGS) reaction scheme, the Patel-Pant model is chosen. The Patel-Pant model expressed the rates of steam reforming and RWGS reactions also in L-H form.

$$r_{\mathrm{SRM}} = \frac{k_r K_{\mathrm{CH_3O^{(1)}}} (P_{\mathrm{CH_3OH}} / P_{\mathrm{H_2}}^{1/2})[1 - (P_{\mathrm{H_2}}^3 P_{\mathrm{CO_2}} / K_r^* P_{\mathrm{CH_3OH}} P_{\mathrm{H_2O}})]}{\left[1 + \frac{K_{\mathrm{CH_3O^{(1)}}} P_{\mathrm{CH_3OH}}}{P_{\mathrm{H_2}}^{1/2}} + \frac{K_{\mathrm{OH^{(1)}}} P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}}^{1/2}} + \frac{K_{\mathrm{CH_3OCHO^{(1)}}} P_{\mathrm{H_2}} P_{\mathrm{CO_2}} P_{\mathrm{CH_3OH}}}{P_{\mathrm{H_2O}}} + K_{\mathrm{HCOO^{(1)}}} P_{\mathrm{H_2}}^{1/2} P_{\mathrm{CO_2}}\right]^2}$$

$$r_{\mathrm{rWGS}} = \frac{k_{rw} K_{\mathrm{HCOO^{(1)}}} (P_{\mathrm{H_2}}^{1/2} P_{\mathrm{CO_2}})[1 - (P_{\mathrm{H_2O}} P_{\mathrm{CO}} / K_{rw}^* P_{\mathrm{H_2}} P_{\mathrm{CO_2}})]}{\left[1 + \frac{K_{\mathrm{CH_3O^{(1)}}} P_{\mathrm{CH_3OH}}}{P_{\mathrm{H_2}}^{1/2}} + \frac{K_{\mathrm{OH^{(1)}}} P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}}^{1/2}} + \frac{K_{\mathrm{CH_3OCHO^{(1)}}} P_{\mathrm{H_2}} P_{\mathrm{CO_2}} P_{\mathrm{CH_3OH}}}{P_{\mathrm{H_2O}}} + K_{\mathrm{HCOO^{(1)}}} P_{\mathrm{H_2}}^{1/2} P_{\mathrm{CO_2}}\right]^2}$$

The empirical expression suggested by both Peppley and Patel are very complex. Thus a very careful technique to calculate the value must be observed. For calculation purposes, the values of constants are directly taken from the respective journals. It is assumed that all those constants values are taken from experimental data which each authors had done in their research.

The calculation is carried out at reaction temperature of 573 K with the constant pressure of 1.0 bar. This is basically the best pressure and temperature in which the catalyst can perform in the optimized way. It is assumed that the reaction between methanol and water as the reactants are 1:1.4. This ratio is chosen to ensure that the reaction can used up all the reactant used and to make sure that higher conversion of methanol could be achieved. The surface area of the catalyst and the amount of catalyst are kept constant for both model.

The calculation is done in a great detail using Microsoft Excel. Since the empirical formula for both models are complex, so the formula is made into chunks to represents every segment in the formula. The value for every chunk will be calculated. After all values of chunks have been calculated, the chunks will be grouped together again to represent the initial complex formula. The value for each expression is then recorded.

It is taken into account that the units for all values are standardised.The value of conversion, flowrate and reaction rate are then calculated at every segment of the reactor. This is done by making arbitrary division for the length of the reactor.

The pseudo-homogeneous plug flow reactor model is assumed and the governing material balance equations for the six components are:

$$\frac{dY_i}{dZ}=\frac{\rho_b A}{F_{i0}}\sum_j \nu_{ij} r_j \ , \ i = \mathrm{CH_3OH, H_2O, CO, CO_2, H_2, N_2}$$

with the initial conditions $Y_i = 0$ at Z = 0 (entry to catalyst bed),

where Y_i = conversion of species *i* per mole of methanol fed, and it is given by

$$F_i = F_{i0} + Y_i F_{M0}$$

Then the component partial pressures in equations (4)-(8) are given by

$$P_i = \frac{F_i}{\sum F_i} P$$

The profiles for the flow rates (F_i's) and the rates of reaction (r_j's) for each of the two models are simulated by solving equations (9) for the rate model (4)-(8) together with expressions for rate parameters, using the Microsoft Excel. The operating parameters of the reactor used for the simulation are given in Table 1.

Table 1. Operating parameters for the simulation of bench reactor

Parameter	Value
Bed density, ρ_b	1500 kg m^{-3}
Surface area of catalyst, S_A	1.0E+5 m^2 kg^{-1}
Bed diameter, D	0.02 m
Bed length, L	0.1 m
Reaction temperature, T	473-573 K
Pressure, P	1.0 bar
Methanol feed rate, F_{M0}	2.0 mmol s^{-1}
Steam/methanol molar feed ratio, R	1.0-1.4
Inert (nitrogen) flow rate	2.0 mmol s^{-1}

CHAPTER 4: RESULT AND DISCUSSION

The result of the simulation will be analyzed to see the relevancy and thermodynamics consistency of each of the model used. Comparison will be made for all models involved and judgment will be made to which model actually lays the best explanation for methanol-steam reformer process.

With the regards to the progress of the research, the student has successfully done the simulation for the first model which is the Peppley *et al.* (1999).The following are the two graphs plotted.

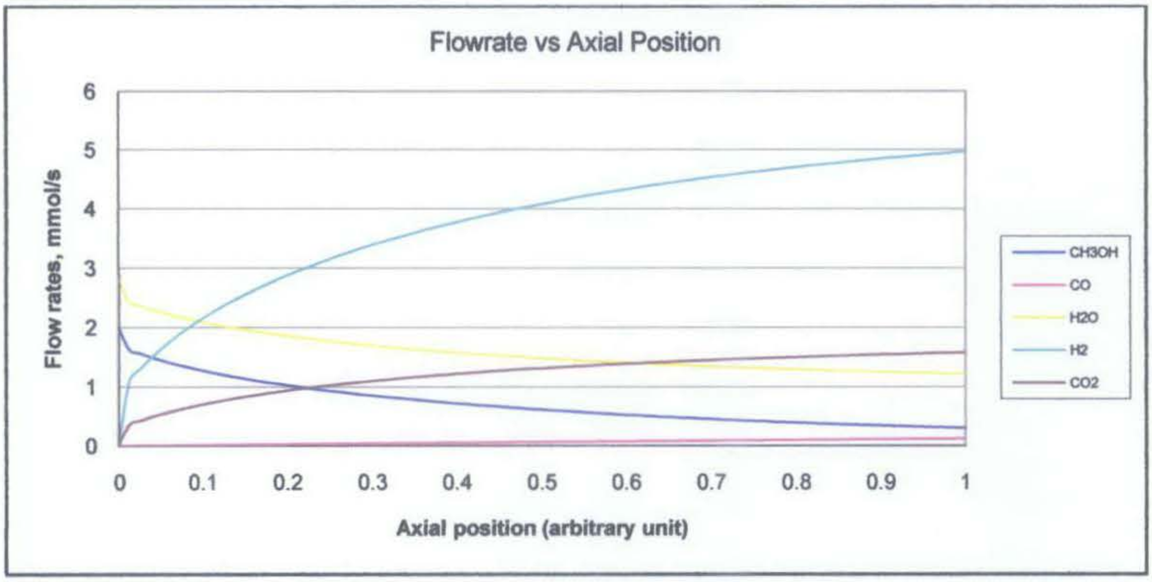

Figure 2: flowrate,F of all components along the plug flow reactor, Z for Peppley model

The graph in figure 2 above is obtained by plotting flowrate of each components species along the axial position of the plug flow reactor. As can be seen from the trend of the graph, the flowrate of hydrogen, H_2 increase significantly as it is the main product in this reaction. The Carbon dioxide, CO_2 is also increasing but the flowrate is not very high compared to the hydrogen. The flowrate of methanol, CH_3OH and water, H_2O show decreasing trend but the graph shows that toward the end of the reactor, they are still exist with certain degree of concentration. It shows that the reactants are not fully consumed. While the poisonous gas carbon monoxide, CO is produced but with a little concentration.

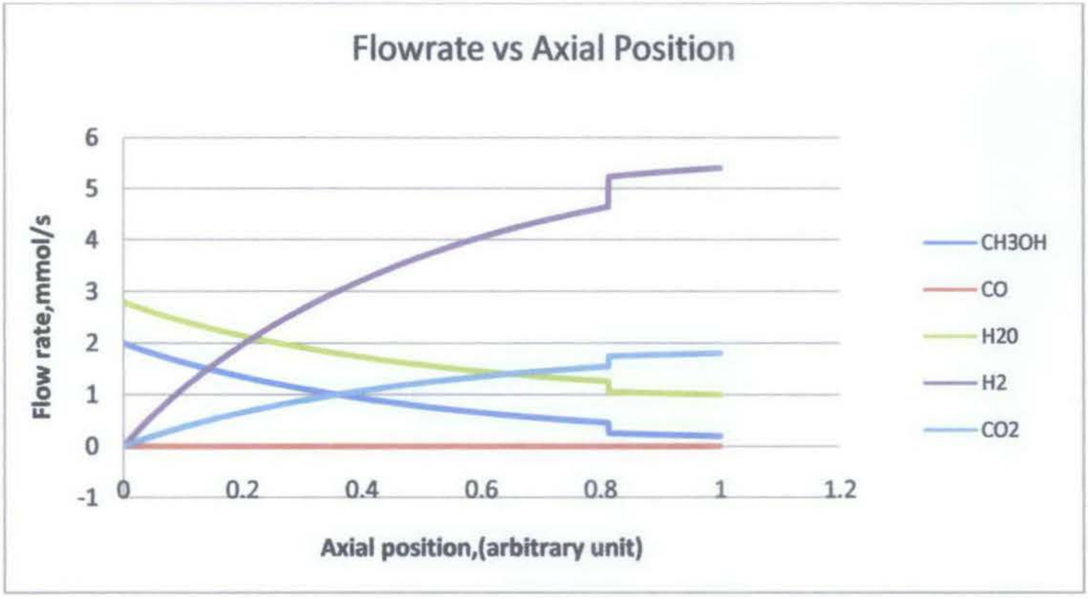

Figure 3: flowrate,F of all components along the plug flow reactor,Z for Patel&Pant model

While for Patel & Pant model, the flowrate of each species along the reactor is tabulated and plotted into a graph as can be seen above.The trend of this graph is almost similar to the Peppley model in figure 2.The flowrate of CH_3OH and H_2O decrease along the species move along the reactor. Flowrate of H_2 increase steadily and later achieve steady flowrate when CH_3OH conversion achieves 90%. Besides, the flowrate of CO_2 and CO are both built up along the reactor. However the flowrate of the CO is very small.

Both models appear to be similar in their flowrate profile.But if we can see the graph closer,the flowrate of H_2 in Peppley Model increase faster compared to Patel&Pant Model.With the regards to the production of poisonous gasous CO, both models yield a small amount of CO in the reactor due to reaction steps occur. However, the amount of CO produced in the latter model is extremely small compared to the one of Peppley. In Peppley model the amount of CO looks significant at the exit of the reactor.

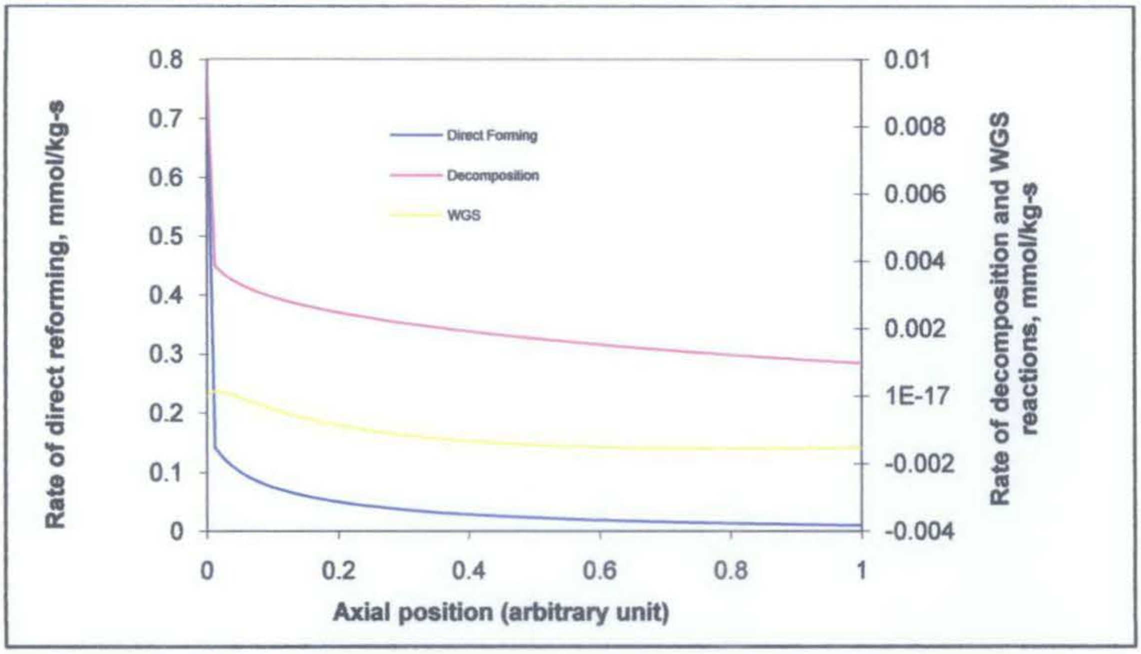

Figure 4: reaction rate, r along the plug flow reactor, Z for Peppley model

The above figure shows the graph of rate of reaction for the three reaction proposed by Peppley *et al* (1999) which are rate of direct reforming,rate of decomposition and also the rate of water gas shift. Initially, in the entrance of the plug flow reactor,The rate for the three reaction is very high as reaction occur at maximum at the entrance. However,the three reaction rate drop sharply after that.The reaction rate for the direct reforming drop to the lowest compared to another to rate of reaction. It dies off in the end part of the reactor. Reaction rate for water gas shift drops lower than the decomposition one. After experiencing drop, the reaction rate of the water gas shift seems to almost constant throughout the reactor. While for reaction rate for decomposition reaction, it experienced the least drop in the rate and throughout the reactor, the reaction rate slowly go down

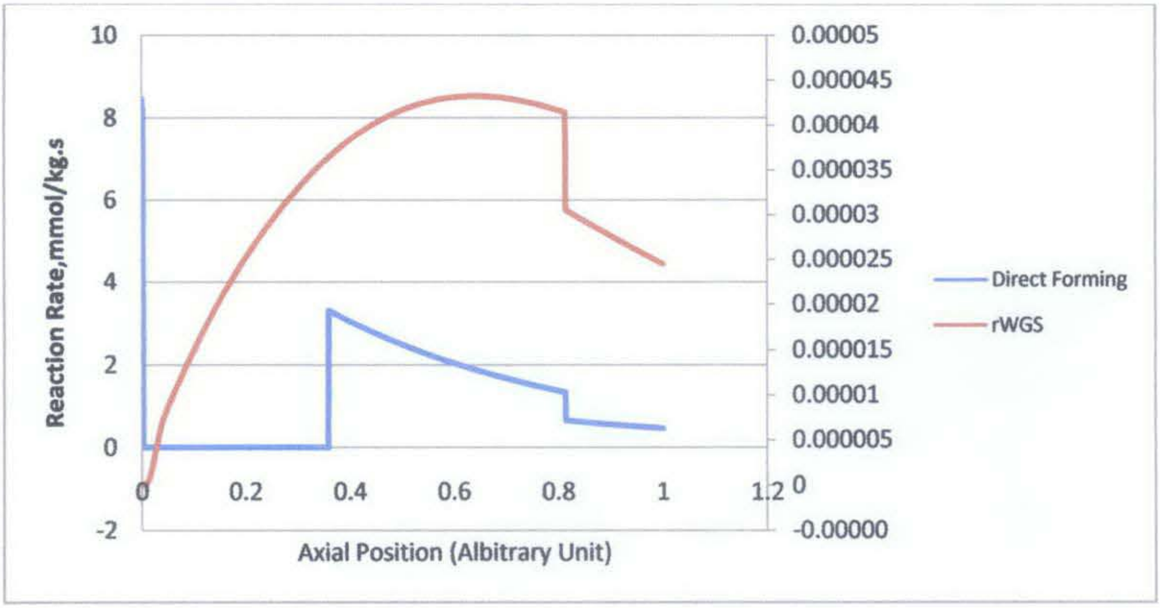

Figure 5: reaction rate, r along the plug flow reactor, Z for Patel & pant model

There is a different story for the Patel & Pant model. As being mentioned earlier, only two reaction steps involved which are direct forming and also the reverse Water Gas Shift (rWGS).From the numerical calculation as well as the trend of the graph itself, it can be said that the reaction of the direct forming of methanol is initially very high.However the reaction rate decreases along the reactor with some sudden increase in the value and end up becoming very low at the outlet of the reactor. This phenomenon occurs because most of the reactants react very fast at the very first part of the reactor. The sudden increase at z=0.4 might due to some error in the model proposed by the author.

When the two models are compared closely several differences are noticed. Firstly the reaction rate for the direct forming in Peppley Model is lower compared to the Patel-Pant. This is not the case in the latter model as the rate is much higher and this lead to faster production of products. The reaction rate for the decomposition part is low and it is decreasing. While for water gas shift reaction (WGS) the reaction rate is negative. This implies that the reaction occurs in the reverse direction or in another words rWGS reaction is actually taking place in the Peppley Model.

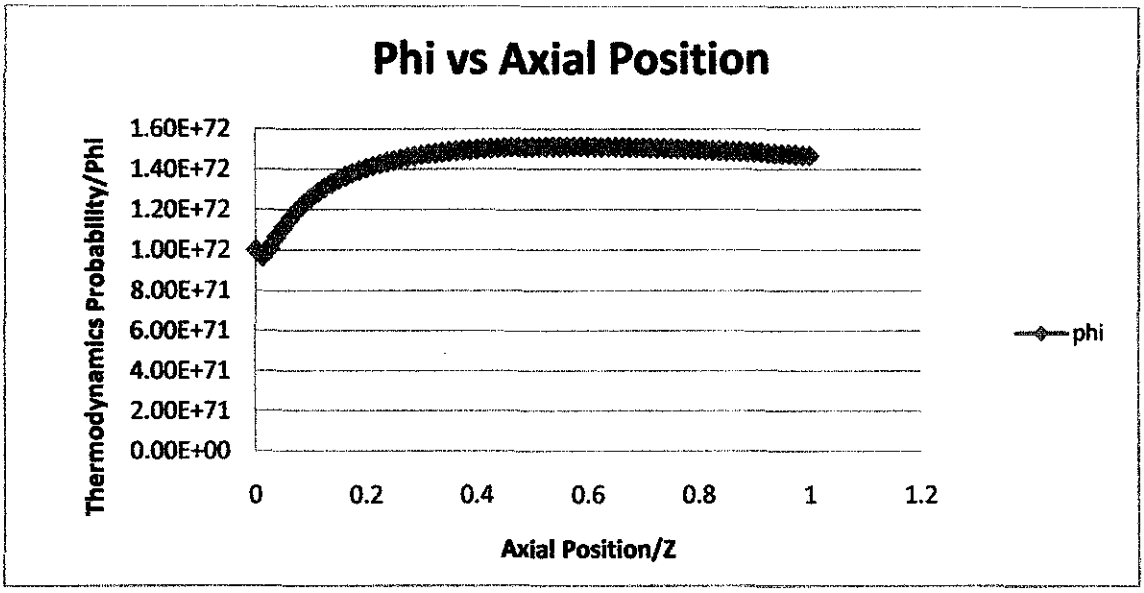

Figure 6: Thermodynamics Probability, Φ along the axial position of the reactor (Peppley Model)

There is another term called Thermodynamics consistency that we must evaluate for both model. This term is more specifically used to see whether a reaction is consistent or not with the thermodynamics principle. The WGS and RWGS reaction are two reactions of the concerned. The term Φ which represent by the following formulas are used to check the thermodynamics probability of both models.

$$\Phi = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O} K_{WGS}} = \frac{F_{CO_2} F_{H_2}}{F_{CO} F_{H_2O} K_{WGS}}$$

According to this fundamental fact, if Φ is less than 1.0, there is a potential for WGS reaction to occur until the equilibrium is reached. If Φ is greater than 1.0, RWGS reaction is thermodynamically favorable. If refer to the figure 6, it shows how the thermodynamic probability change across the axial position of the reactor for Peppley Model. It is found all values of Φ is very large and exceed 1.0. This implies that there is no potential for WGS reaction to occur and the RWGS is likely to occur in the reaction. This is proven by the reaction rate profile of the WGS reaction which is negative in values. This further proves that reaction has been going on in reverse direction for the WGS reaction.

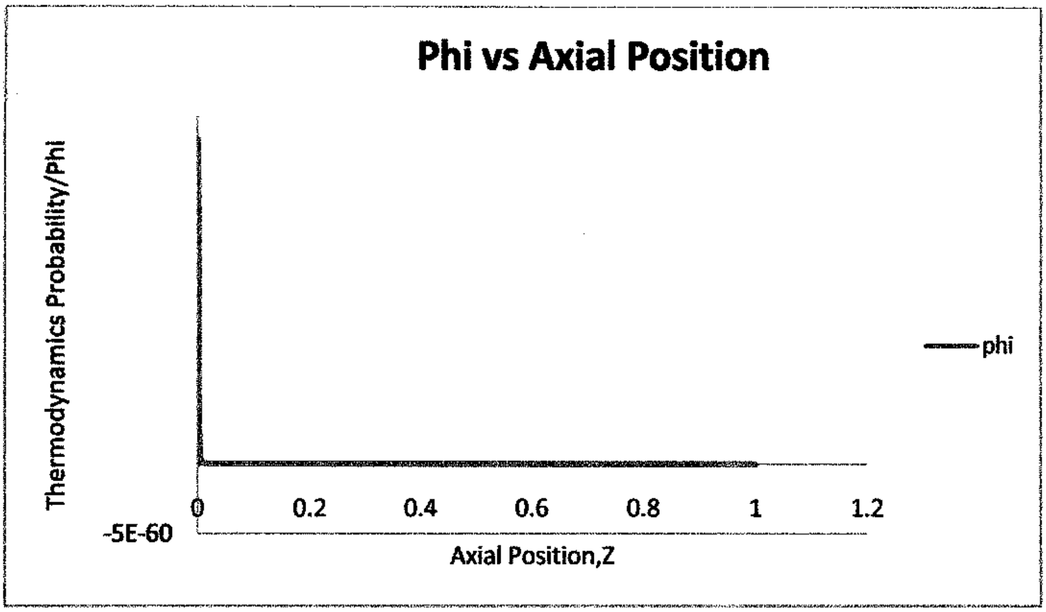

Figure 7: Thermodynamics Probability, Φ along the axial position of the reactor (Patel&Pant Model)

Figure 7 shows thermodynamics probability, Φ for Patel-Pant Model along the reactor for this reaction. From the graph, we can conclude that the value of this thermodynamic is not consistent. Initially the value is extremely large, which gives us indication that the RWGS reaction to occur. However, the value of phi drops abruptly afterwards until reaching the exit of the reactor. This shows that inconsistency happen in this model. Sometimes it favors WGS reaction but some other times it favors RWGS reaction. The reaction rate profile for RWGS reaction confirms that reaction rate values are all positives. This further proves that the model is inconsistent.

CHAPTER 5: CONCLUSION & RECOMMENDATION

From the result of the simulation, it is concluded that the Peppley Model is better if compared to the Patel-Pant Model. The Peppley Model seems to be more robust. It is because the model is consistent with the local thermodynamic. The Patel-Pant Model has got inconsistency in it, though it shows some better characteristics compared to the one of Peppey such as in the flowrate profile as well as in the least production of the carbon monoxide gas, CO.

However, the Peppley model needs to be modified to make it a better model. The rate expression need to be further simplified as the one proposed by Purnama *et. al* (2004). Last but not least, the WGS reaction rate expression must be changed so that it can suit the RWGS trend that is actually happening in the Peppley Model.

From this observation, a modified kinetic model should have the following characteristics;

- It must contain the minimum number of reactions involving the primary components of reaction mixture; CH_3OH,H_2O,CO,CO_2, and H_2
- Contain rate expression for RWGS rather than WGS, by reversing the Peppley expression for WGS, which is thermodynamically consistent.
- Simple rate expression for reforming as given by Lee et al. by incorporating the reverse rate term for thermodynamic consistency.
- Simplified rate expression for WGS obtained in part 2 above by using the same reasoning as Lee at all.

The following equation from the Lee model is proposed for the modified expression of Peppley model;

$$r_{SRM} = \frac{K_{SR}K_M\left(P_M/\sqrt{P_H}\right)\left(1-P_H^3P_C/K_{SR}P_MP_W\right)}{1+K_M\left(P_M/\sqrt{P_H}\right)\left(1+\sqrt{K_HP_H}\right)} \quad . \quad . \quad . \quad . \quad . \qquad 1$$

$$r_{RWGS} = \frac{K_{RWGS}P_HP_{CO2}\left(1-P_{CO}P_W/P_{CO2}P_HK_{RWGS}\right)}{\left[1+K_M\left(P_M/\sqrt{P_H}\right)+K_{OH}\left(P_W/\sqrt{P_H}\right)\right]2} \quad . \quad . \quad . \quad . \quad . \qquad 2$$

NOTATION

C_T	total surface concentration of site S_1, mol m^{-2}
C_{S1}	vacant site concentration of site S_1, mol m^{-2}
D	reactor inner diameter, mm
Dp	catalyst particle size, mm
E_i	activation energy for rate constant of reaction i, kJ mol^{-1}
F	molar flow rate of methanol, mol s^{-1}
ΔH_i	heat of adsorption for surface species i or heat of reaction for formation of surface species i, kJ mol^{-1}
L	catalyst bed height, mm
K_i	equilibrium constant of reaction i or adsorption coefficient for surface species i
k_i	rate constant for reaction i; units will be specific to the form of the rate expression
k_i^{∞}	pre exponential rate constant for reaction i, m^2 s^{-1} mol^{-1}
P	operating pressure, atm
P_i	partial pressure of component i, atm
r_i	rate of reaction of component i, mol m^2 s^{-1}
ΔS_i	entropy of adsorption for species i, J mol^{-1} K^{-1}
T	temperature, K
T_m	mean temperature, K
W	mass of catalyst, kg

Subscripts

r	methanol steam reforming reaction
rw	reverse water gas shift reaction
i	Reaction or product species

REFERENCES

1. Agrell, J., K. Hasselbo, K. Jansson, S. G. Jaras and M. Boutonnet (2001). *Production of hydrogen from methanol over Cu/ZnO catalysts promoted by ZrO_2 and Al_2O_3*. Appl. Catal. A: General, 211, 239

2. Brant A. Peppley, J. C. (1998). Applied Catalyst. *Methanol-steam reforming on Cu/ZnO/Al2O3 catalysts A comprehensive kinetic model*, 1.

3. Busca, G., Costantino, U., Marmottini, F., Montanari, T., Patrono, P., Pinzari, F., Ramis, G., 2006. *Methanol steam reforming over ex-hydrotalcite Cu–Zn–Al catalysts*. Applied Catalysis A: General 310, 70–78.

4. Breen, J.P., Meunier, F.C., Ross, J.R.H., 1999. *Mechanistic aspects of the steam reforming of methanol over a CuO/ZnO/ZrO2/Al2O3 catalyst.* Chemical Communications.

5. Weiqiang Cao,Guangwen Shulian Li, Quan Yuan (2006). Methanol-steam reforming over a ZnO–Cr2O3/CeO2–ZrO2/Al2O3 catalyst. Chemical Engineering Journal; 93-97.

6. Elio E. Gonzo. (2007). Hydrogen from methanol-steam reforming. *International Journal of Hydrogen Energy* : 1-3

7. Fausto Gallucci, A. B. (2006). Co-current and counter-current modes for methanol steam. *International Journal of Hydrogen Energy* :1-4

8. G. Arzamendi, P. D. (2008). Integration of methanol steam reforming and combustion in a microchannel. *Catalyst Today* :1-5

9. Guido Buzzi-Ferraris and Flavio Manenti (2008), *Kinetic Models Analysis*. Chem. Eng. Sci, 1, 1062

10. Helfferich, F. (2004). *Kinetics of Multispteps Reactions 2nd Edition.* (N. Green, Ed.) London,England: Elsevier: 1-6

11. Hou, K., Hughes, R., 2001. *The kinetics of methane steam reforming over a Ni/a–Al2O3 catalyst.*Chemical Engineering Journal 82, 311–328

12. Jiang, C.J., Trimm, D.L., Wainwright, M.S., 1993b. *Kinetic study of steam reforming of methanol over copper-based catalysts*. Applied Catalysis A: General 93, 245–255.

13. Kajornsak Faungnawakij, Ryuji Kikuchi,Koichi Eguchi (2006).*Thermodynamic evaluation of methanol steam reforming for hydrogen production.* Journal of Power Sources; 86-94.

14. Liwei Pan, Shudong Wang(2005).*Modeling of a compact plate-fin reformer for methanol steam reforming in fuel cell systems.* Chemical Engineering Journal; 51-53.

15. Lee, J. K., J. B. Ko and D. H. Kim (2004). *Methanol steam reforming over $Cu/ZnO/Al_2O_3$ catalyst: kinetic and effectiveness factor*. Appl. Catal. A: General, 278, 25-27.

16. L.M. Keams, J.C. Amphlett, E. Haliop, H.M. Jenkins, R.F. Mann and B.A. Peppley (2009). *Hydrogen Production via Methanol - Steam Reforming using Catalysts containing a Hydrotalcite Phase Structure.* Department of Chemistry and Chemical Engineering Royal Military College of Canada; 904-907

17. Peterson, T.I., Lapidus, L., 1966. *Nonlinear estimation analysis of the kinetics of catalytic ethanol dehydrogenation.* Chemical Engineering Science 21:1-6

18. Purnama, H., T. Ressler, R. E. Jentoft, H. Soerijanto, R. Schlogl and R. Schomacker (2004). *CO formation/selectivity for steam reforming of methanol with a commercial* *$CuO/ZnO/Al_2O_3$* catalyst. Appl. Catal. A: General, 259, 83-85

19. Rick B. Watson, P. M. (1999). *Alcohol Steam Reforming for Hydrogen Production.* 1.

20. Sanjay Patel, K.K Pant (2009). Applied Catalysis A: General. *Kinetic Modeling of oxidative steam reforming of methanol over Cu/ZnO/CeO2/Al2O3 catalyst*, 189-193.

21. Weiqiang Caoa, G. (2006). Methanol-steam reforming over a ZnO–Cr2O3/CeO2–ZrO2/Al2O3 catalyst. *Chemical Engineering Journal*, 4.

22. Yan, X., Wang, S., Li, X., Hou, M., Yuan, Z., Li, D., Pan, L., Zhang, C.,Liu, J., Ming, P., Yi, B., 2006. A 75-kW *methanol reforming fuel cell system.* Journal of Power Sources 244, 1–9.

APPENDIX 1

a) Data tabulated for the Flowrate,F of Species along the reactor,Z (Peppley Model)

z	F1	F2	F3	F4	F5	Φ
0	2	0	2.8	0	0	1.00000E+72
0.0125	1.632963	0.004622	2.437585806	1.096487	0.362414	9.65037E+71
0.025	1.564626	0.00637	2.370995293	1.299753	0.429005	1.01029E+72
0.0375	1.504484	0.008029	2.312513342	1.478518	0.487487	1.06222E+72
0.05	1.450445	0.009642	2.260086849	1.639023	0.539913	1.1112E+72
0.0625	1.401204	0.01123	2.212434112	1.785157	0.587566	1.15521E+72
0.075	1.355877	0.012805	2.168682017	1.919563	0.631318	1.19413E+72
0.0875	1.313826	0.014374	2.128200025	2.044147	0.6718	1.2284E+72
0.1	1.274573	0.01594	2.090513228	2.160341	0.709487	1.25858E+72
0.1125	1.237745	0.017507	2.055252366	2.269257	0.744748	1.28522E+72
0.125	1.203048	0.019075	2.022123051	2.371781	0.777877	1.30879E+72
0.1375	1.17024	0.020645	1.990885789	2.468633	0.809114	1.32973E+72
0.15	1.139125	0.022217	1.961342459	2.560407	0.838658	1.34838E+72
0.1625	1.109535	0.023791	1.933326843	2.647602	0.866673	1.36504E+72
0.175	1.081331	0.025367	1.906697802	2.730641	0.893302	1.37998E+72
0.1875	1.05439	0.026944	1.881334234	2.809886	0.918666	1.39341E+72
0.2	1.028609	0.028522	1.857131286	2.885651	0.942869	1.4055E+72
0.2125	1.003897	0.030101	1.833997434	2.958209	0.966003	1.41643E+72
0.225	0.980173	0.03168	1.811852218	3.027802	0.988148	1.42631E+72
0.2375	0.957367	0.033258	1.790624453	3.094642	1.009376	1.43526E+72
0.25	0.935415	0.034835	1.770250791	3.158918	1.029749	1.44338E+72
0.2625	0.914263	0.036412	1.750674561	3.220799	1.049325	1.45075E+72
0.275	0.893859	0.037986	1.731844828	3.280438	1.068155	1.45746E+72
0.2875	0.874157	0.039559	1.713715607	3.337971	1.086284	1.46355E+72
0.3	0.855116	0.041129	1.696245219	3.393523	1.103755	1.4691E+72
0.3125	0.836699	0.042697	1.679395744	3.447206	1.120604	1.47414E+72
0.325	0.818872	0.044261	1.663132565	3.499124	1.136867	1.47872E+72
0.3375	0.801602	0.045822	1.647423982	3.549372	1.152576	1.48288E+72
0.35	0.784862	0.047379	1.632240876	3.598036	1.167759	1.48665E+72
0.3625	0.768624	0.048933	1.617556428	3.645196	1.182444	1.49007E+72
0.375	0.752864	0.050482	1.603345872	3.690926	1.196654	1.49316E+72
0.3875	0.73756	0.052026	1.589586283	3.735294	1.210414	1.49595E+72
0.4	0.72269	0.053566	1.576256392	3.778363	1.223744	1.49845E+72
0.4125	0.708235	0.055101	1.563336423	3.820193	1.236664	1.50068E+72
0.425	0.694177	0.056631	1.550807951	3.860838	1.249192	1.50267E+72
0.4375	0.680499	0.058155	1.53865378	3.900349	1.261346	1.50444E+72
0.45	0.667184	0.059674	1.526857826	3.938774	1.273142	1.50598E+72
0.4625	0.654218	0.061187	1.515405025	3.976158	1.284595	1.50733E+72
0.475	0.641587	0.062694	1.504281243	4.012544	1.295719	1.50849E+72
0.4875	0.629278	0.064195	1.493473198	4.04797	1.306527	1.50946E+72
0.5	0.617279	0.06569	1.48296839	4.082474	1.317032	1.51027E+72
0.5125	0.605577	0.067178	1.472755039	4.116091	1.327245	1.51093E+72
0.525	0.594162	0.06866	1.462822031	4.148854	1.337178	1.51143E+72

0.5375	0.583024	0.070135	1.453158862	4.180794	1.346841	1.51179E+72
0.55	0.572152	0.071604	1.443755596	4.21194	1.356244	1.51201E+72
0.5625	0.561538	0.073065	1.434602822	4.242322	1.365397	1.51211E+72
0.575	0.551172	0.07452	1.425691619	4.271965	1.374308	1.51209E+72
0.5875	0.541046	0.075968	1.417013517	4.300894	1.382986	1.51196E+72
0.6	0.531153	0.077408	1.408560468	4.329135	1.39144	1.51171E+72
0.6125	0.521484	0.078841	1.40032482	4.356708	1.399675	1.51136E+72
0.625	0.512032	0.080267	1.392299286	4.383636	1.407701	1.51091E+72
0.6375	0.502791	0.081685	1.384476923	4.40994	1.415523	1.51037E+72
0.65	0.493755	0.083096	1.37685111	4.435639	1.423149	1.50974E+72
0.6625	0.484916	0.0845	1.369415529	4.460753	1.430584	1.50902E+72
0.675	0.476269	0.085896	1.362164141	4.485299	1.437836	1.50822E+72
0.6875	0.467807	0.087284	1.355091176	4.509294	1.444909	1.50734E+72
0.7	0.459527	0.088664	1.348191111	4.532755	1.451809	1.50639E+72
0.7125	0.451422	0.090037	1.341458661	4.555697	1.458541	1.50536E+72
0.725	0.443487	0.091401	1.33488876	4.578137	1.465111	1.50427E+72
0.7375	0.435718	0.092758	1.328476553	4.600087	1.471523	1.50311E+72
0.75	0.42811	0.094107	1.322217381	4.621562	1.477783	1.50189E+72
0.7625	0.420659	0.095448	1.316106772	4.642576	1.483893	1.50061E+72
0.775	0.413359	0.096781	1.310140431	4.663141	1.48986	1.49927E+72
0.7875	0.406208	0.098106	1.304314228	4.68327	1.495686	1.49787E+72
0.8	0.399201	0.099423	1.298624195	4.702974	1.501376	1.49643E+72
0.8125	0.392335	0.100732	1.293066509	4.722264	1.506933	1.49493E+72
0.825	0.385605	0.102033	1.287637495	4.741153	1.512363	1.49338E+72
0.8375	0.379008	0.103325	1.282333609	4.75965	1.517666	1.49179E+72
0.85	0.372542	0.10461	1.277151438	4.777765	1.522849	1.49016E+72
0.8625	0.366202	0.105886	1.272087691	4.795509	1.527912	1.48848E+72
0.875	0.359985	0.107154	1.267139191	4.81289	1.532861	1.48676E+72
0.8875	0.353889	0.108414	1.262302877	4.829919	1.537697	1.485E+72
0.9	0.34791	0.109666	1.257575789	4.846604	1.542424	1.48321E+72
0.9125	0.342046	0.110909	1.252955069	4.862953	1.547045	1.48138E+72
0.925	0.336294	0.112144	1.248437958	4.878974	1.551562	1.47951E+72
0.9375	0.330651	0.113371	1.244021786	4.894677	1.555978	1.47762E+72
0.95	0.325114	0.11459	1.239703972	4.910068	1.560296	1.47569E+72
0.9625	0.319682	0.1158	1.235482019	4.925155	1.564518	1.47373E+72
0.975	0.314351	0.117003	1.231353511	4.939945	1.568646	1.47175E+72
0.9875	0.309119	0.118197	1.227316107	4.954445	1.572684	1.46974E+72
1	0.303985	0.119382	1.223367541	4.968662	1.576632	1.4677E+72

b) Data tabulated for the reaction rate,r of the three different reactions along the reactor axial position,Z (Peppley Model)

z	rate1	rate2	rate3
0	0.769065	0.009809	0
0.0125	0.141166	0.003851	0.000144
0.025	0.123991	0.003632	0.000111
0.0375	0.111211	0.003464	4.15E-05
0.05	0.101164	0.003328	-4.2E-05
0.0625	0.092974	0.003212	-0.00013
0.075	0.086122	0.003113	-0.00022
0.0875	0.080274	0.003024	-0.0003
0.1	0.075206	0.002945	-0.00038
0.1125	0.070758	0.002873	-0.00046
0.125	0.066813	0.002806	-0.00053
0.1375	0.063284	0.002744	-0.00059
0.15	0.060104	0.002687	-0.00065
0.1625	0.05722	0.002632	-0.00071
0.175	0.054589	0.002581	-0.00077
0.1875	0.052176	0.002533	-0.00082
0.2	0.049955	0.002486	-0.00086
0.2125	0.047902	0.002442	-0.00091
0.225	0.045997	0.002399	-0.00095
0.2375	0.044223	0.002358	-0.00099
0.25	0.042568	0.002319	-0.00103
0.2625	0.041018	0.002281	-0.00106
0.275	0.039565	0.002244	-0.00109
0.2875	0.038197	0.002208	-0.00112
0.3	0.036908	0.002173	-0.00115
0.3125	0.035692	0.00214	-0.00118
0.325	0.03454	0.002107	-0.00121
0.3375	0.033449	0.002075	-0.00123
0.35	0.032414	0.002043	-0.00125
0.3625	0.03143	0.002013	-0.00127
0.375	0.030493	0.001983	-0.00129
0.3875	0.029601	0.001954	-0.00131
0.4	0.028749	0.001925	-0.00133
0.4125	0.027935	0.001897	-0.00135
0.425	0.027157	0.00187	-0.00137
0.4375	0.026412	0.001843	-0.00138
0.45	0.025698	0.001816	-0.00139
0.4625	0.025013	0.00179	-0.00141
0.475	0.024356	0.001765	-0.00142
0.4875	0.023724	0.00174	-0.00143
0.5	0.023117	0.001715	-0.00144
0.5125	0.022532	0.001691	-0.00145
0.525	0.021969	0.001667	-0.00146
0.5375	0.021427	0.001644	-0.00147

0.55	0.020904	0.00162	-0.00148
0.5625	0.020399	0.001598	-0.00149
0.575	0.019912	0.001575	-0.0015
0.5875	0.019441	0.001553	-0.0015
0.6	0.018986	0.001532	-0.00151
0.6125	0.018546	0.00151	-0.00152
0.625	0.01812	0.001489	-0.00152
0.6375	0.017708	0.001468	-0.00153
0.65	0.017309	0.001448	-0.00153
0.6625	0.016922	0.001428	-0.00153
0.675	0.016547	0.001408	-0.00154
0.6875	0.016183	0.001388	-0.00154
0.7	0.01583	0.001369	-0.00154
0.7125	0.015488	0.00135	-0.00155
0.725	0.015155	0.001331	-0.00155
0.7375	0.014832	0.001313	-0.00155
0.75	0.014518	0.001294	-0.00155
0.7625	0.014213	0.001276	-0.00155
0.775	0.013917	0.001259	-0.00155
0.7875	0.013628	0.001241	-0.00155
0.8	0.013347	0.001224	-0.00155
0.8125	0.013074	0.001207	-0.00155
0.825	0.012808	0.00119	-0.00155
0.8375	0.012549	0.001173	-0.00155
0.85	0.012297	0.001157	-0.00155
0.8625	0.012051	0.001141	-0.00155
0.875	0.011812	0.001125	-0.00155
0.8875	0.011578	0.001109	-0.00155
0.9	0.011351	0.001093	-0.00155
0.9125	0.011129	0.001078	-0.00154
0.925	0.010912	0.001063	-0.00154
0.9375	0.010701	0.001048	-0.00154
0.95	0.010495	0.001033	-0.00154
0.9625	0.010294	0.001019	-0.00153
0.975	0.010097	0.001004	-0.00153
0.9875	0.009905	0.00099	-0.00153
1	0.009718	0.000976	-0.00152

APPENDIX 2

a)Data tabulated for the Flowrate,F of Species along the reactor,Z (Patel & Pant Model)

z	F1	F2	F3	F4	F5	Φ
0	2	0	2.8	0	0	∞
0.000851	1.996012	0	2.796012	0.011963	0.003988	∞
0.001702	1.992119	2.84E-14	2.792119	0.023643	0.007881	2.33E-59
0.002553	1.988268	3.34E-13	2.788268	0.035197	0.011732	4.41E-60
0.003404	1.98445	1.55E-12	2.78445	0.046651	0.01555	1.67E-60
0.004255	1.98066	4.8E-12	2.78066	0.058021	0.01934	8.36E-61
0.005106	1.976895	1.17E-11	2.776895	0.069314	0.023105	4.9E-61
0.005957	1.973154	2.44E-11	2.773154	0.080537	0.026846	3.17E-61
0.006809	1.969435	4.58E-11	2.769435	0.091695	0.030565	2.19E-61
0.00766	1.965736	7.91E-11	2.765736	0.102792	0.034264	1.6E-61
0.008511	1.962056	1.28E-10	2.762056	0.113831	0.037944	1.21E-61
0.009362	1.958395	1.98E-10	2.758395	0.124814	0.041605	9.46E-62
0.010213	1.954752	2.92E-10	2.754752	0.135745	0.045248	7.58E-62
0.011064	1.951125	4.17E-10	2.751125	0.146624	0.048875	6.2E-62
0.011915	1.947515	5.78E-10	2.747515	0.157455	0.052485	5.17E-62
0.012766	1.943921	7.82E-10	2.743921	0.168238	0.056079	4.37E-62
0.013617	1.940342	1.03E-09	2.740342	0.178975	0.059658	3.74E-62
0.014468	1.936777	1.34E-09	2.736777	0.189668	0.063223	3.25E-62
0.015319	1.933228	1.71E-09	2.733228	0.200316	0.066772	2.84E-62
0.01617	1.929692	2.14E-09	2.729692	0.210923	0.070308	2.52E-62
0.017021	1.926171	2.65E-09	2.726171	0.221488	0.073829	2.24E-62
0.017872	1.922663	3.25E-09	2.722663	0.232012	0.077337	2.02E-62
0.018723	1.919167	3.92E-09	2.719167	0.242498	0.080833	1.83E-62
0.019574	1.915685	4.69E-09	2.715685	0.252944	0.084315	1.66E-62
0.020426	1.912216	5.56E-09	2.712216	0.263352	0.087784	1.52E-62
0.021277	1.908759	6.52E-09	2.708759	0.273724	0.091241	1.4E-62
0.022128	1.905314	7.59E-09	2.705314	0.284058	0.094686	1.3E-62
0.022979	1.901881	8.77E-09	2.701881	0.294357	0.098119	1.21E-62
0.02383	1.89846	1.01E-08	2.69846	0.30462	0.10154	1.13E-62
0.024681	1.89505	1.15E-08	2.69505	0.314849	0.10495	1.06E-62
0.025532	1.891652	1.3E-08	2.691652	0.325044	0.108348	1E-62
0.026383	1.888265	1.46E-08	2.688265	0.335205	0.111735	9.46E-63
0.027234	1.884889	1.64E-08	2.684889	0.345333	0.115111	8.97E-63
0.028085	1.881524	1.83E-08	2.681524	0.355428	0.118476	8.54E-63
0.028936	1.87817	2.02E-08	2.67817	0.365491	0.12183	8.16E-63
0.029787	1.874826	2.24E-08	2.674826	0.375522	0.125174	7.81E-63
0.030638	1.871493	2.46E-08	2.671493	0.385522	0.128507	7.5E-63
0.031489	1.868169	2.69E-08	2.66817	0.395492	0.13183	7.22E-63
0.03234	1.864857	2.93E-08	2.664857	0.40543	0.135143	6.96E-63
0.033191	1.861554	3.19E-08	2.661554	0.415339	0.138446	6.73E-63
0.95234	0.212327	2.45E-05	1.012351	5.362995	1.787649	3.84E-63
0.953191	0.21209	2.45E-05	1.012114	5.363707	1.787886	3.84E-63
0.954043	0.211853	2.45E-05	1.011877	5.364417	1.788123	3.84E-63

0.954894	0.211616	2.45E-05	1.011641	5.365126	1.788359	3.84E-63
0.955745	0.21138	2.45E-05	1.011405	5.365835	1.788595	3.84E-63
0.956596	0.211145	2.46E-05	1.011169	5.366542	1.788831	3.84E-63
0.957447	0.210909	2.46E-05	1.010934	5.367247	1.789066	3.84E-63
0.958298	0.210674	2.46E-05	1.010699	5.367952	1.789301	3.84E-63
0.959149	0.21044	2.46E-05	1.010464	5.368656	1.789536	3.84E-63
0.96	0.210206	2.46E-05	1.01023	5.369358	1.78977	3.84E-63
0.960851	0.209972	2.46E-05	1.009996	5.37006	1.790004	3.84E-63
0.961702	0.209738	2.46E-05	1.009763	5.37076	1.790237	3.84E-63
0.962553	0.209505	2.46E-05	1.00953	5.371459	1.79047	3.84E-63
0.963404	0.209273	2.47E-05	1.009297	5.372157	1.790703	3.84E-63
0.964255	0.20904	2.47E-05	1.009065	5.372854	1.790935	3.84E-63
0.965106	0.208808	2.47E-05	1.008833	5.37355	1.791167	3.84E-63
0.965957	0.208577	2.47E-05	1.008601	5.374245	1.791399	3.84E-63
0.966809	0.208346	2.47E-05	1.00837	5.374939	1.79163	3.84E-63
0.96766	0.208115	2.47E-05	1.008139	5.375631	1.791861	3.84E-63
0.968511	0.207884	2.47E-05	1.007909	5.376323	1.792091	3.84E-63
0.969362	0.207654	2.47E-05	1.007679	5.377013	1.792321	3.84E-63
0.970213	0.207424	2.47E-05	1.007449	5.377702	1.792551	3.84E-63
0.971064	0.207195	2.48E-05	1.00722	5.378391	1.79278	3.84E-63
0.971915	0.206966	2.48E-05	1.006991	5.379078	1.793009	3.84E-63
0.972766	0.206737	2.48E-05	1.006762	5.379764	1.793238	3.84E-63
0.973617	0.206509	2.48E-05	1.006534	5.380449	1.793466	3.84E-63
0.974468	0.206281	2.48E-05	1.006306	5.381133	1.793694	3.84E-63
0.975319	0.206053	2.48E-05	1.006078	5.381815	1.793922	3.84E-63
0.97617	0.205826	2.48E-05	1.005851	5.382497	1.794149	3.84E-63
0.977021	0.205599	2.48E-05	1.005624	5.383178	1.794376	3.84E-63
0.977872	0.205373	2.49E-05	1.005397	5.383857	1.794603	3.84E-63
0.978723	0.205146	2.49E-05	1.005171	5.384536	1.794829	3.84E-63
0.979574	0.204921	2.49E-05	1.004946	5.385213	1.795054	3.84E-63
0.980426	0.204695	2.49E-05	1.00472	5.385889	1.79528	3.84E-63
0.981277	0.20447	2.49E-05	1.004495	5.386565	1.795505	3.84E-63
0.982128	0.204245	2.49E-05	1.00427	5.387239	1.79573	3.84E-63
0.982979	0.204021	2.49E-05	1.004046	5.387912	1.795954	3.84E-63
0.98383	0.203797	2.49E-05	1.003822	5.388584	1.796178	3.84E-63
0.984681	0.203573	2.5E-05	1.003598	5.389255	1.796402	3.84E-63
0.985532	0.20335	2.5E-05	1.003375	5.389925	1.796625	3.84E-63
0.986383	0.203127	2.5E-05	1.003152	5.390594	1.796848	3.84E-63
0.987234	0.202904	2.5E-05	1.002929	5.391262	1.797071	3.84E-63
0.988085	0.202682	2.5E-05	1.002707	5.391929	1.797293	3.84E-63
0.988936	0.20246	2.5E-05	1.002485	5.392594	1.797515	3.84E-63
0.989787	0.202239	2.5E-05	1.002264	5.393259	1.797736	3.84E-63
0.990638	0.202017	2.5E-05	1.002043	5.393922	1.797957	3.84E-63
0.991489	0.201797	2.5E-05	1.001822	5.394585	1.798178	3.84E-63
0.99234	0.201576	2.51E-05	1.001601	5.395247	1.798399	3.84E-63
0.993191	0.201356	2.51E-05	1.001381	5.395907	1.798619	3.84E-63
0.994043	0.201136	2.51E-05	1.001161	5.396566	1.798839	3.84E-63
0.994894	0.200917	2.51E-05	1.000942	5.397225	1.799058	3.84E-63

0.995745	0.200698	2.51E-05	1.000723	5.397882	1.799277	3.84E-63
0.996596	0.200479	2.51E-05	1.000504	5.398539	1.799496	3.84E-63
0.997447	0.20026	2.51E-05	1.000285	5.399194	1.799715	3.84E-63
0.998298	0.200042	2.51E-05	1.000067	5.399848	1.799933	3.84E-63
0.999149	0.199825	2.51E-05	0.99985	5.400501	1.80015	3.84E-63
1	0.199607	2.52E-05	0.999632	5.401153	1.800368	3.84E-63

b) Data tabulated for the reaction rate,r of the three different reactions along the reactor axial position,Z (Patel & Pant)

Z	rateSRM	rate RWGS
0	8.462366776	0
0.000851	8.26132248	6.03383E-11
0.001702	8.172711381	6.48154E-10
0.002553	4.1399E-05	2.5873E-09
0.003404	4.13823E-05	6.88102E-09
0.004255	3.11321E-05	1.46436E-08
0.005106	3.11038E-05	2.70557E-08
0.005957	3.10756E-05	4.53283E-08
0.006809	3.10473E-05	7.06707E-08
0.00766	3.10191E-05	1.04261E-07
0.008511	3.09909E-05	1.4722E-07
0.009362	3.09626E-05	2.00584E-07
0.010213	3.09344E-05	2.6528E-07
0.011064	3.09061E-05	3.42109E-07
0.011915	3.08779E-05	4.31724E-07
0.012766	3.08496E-05	5.34616E-07
0.013617	3.08214E-05	6.51103E-07
0.014468	3.07931E-05	7.81321E-07
0.015319	3.07649E-05	9.25219E-07
0.01617	3.07367E-05	1.08256E-06
0.017021	3.07084E-05	1.25293E-06
0.017872	3.06802E-05	1.43574E-06
0.018723	3.06519E-05	1.63023E-06
0.019574	3.06237E-05	1.83551E-06
0.020426	3.05954E-05	2.05055E-06
0.021277	3.05672E-05	2.2742E-06
0.022128	4.09996E-05	2.50525E-06
0.022979	4.09815E-05	2.74242E-06
0.02383	4.09634E-05	2.98437E-06
0.024681	4.09452E-05	3.22978E-06
0.025532	4.09269E-05	3.47732E-06
0.026383	4.09087E-05	3.7257E-06
0.027234	4.08903E-05	3.97367E-06
0.028085	4.08719E-05	4.22007E-06
0.028936	4.08534E-05	4.46384E-06
0.029787	4.08349E-05	4.70398E-06

0.030638	4.08163E-05	4.93964E-06
0.031489	4.07977E-05	5.17008E-06
0.03234	4.0779E-05	5.39468E-06
0.033191	4.07603E-05	5.61295E-06
0.944681	0.510517618	2.62418E-05
0.945532	0.509708388	2.62145E-05
0.946383	0.508900497	2.61872E-05
0.947234	0.508093941	2.616E-05
0.948085	0.507288718	2.61327E-05
0.948936	0.506484827	2.61055E-05
0.949787	0.505682264	2.60782E-05
0.950638	0.504881028	2.6051E-05
0.951489	0.504081116	2.60238E-05
0.95234	0.503282525	2.59966E-05
0.953191	0.502485254	2.59694E-05
0.954043	0.5016893	2.59422E-05
0.954894	0.50089466	2.5915E-05
0.955745	0.500101334	2.58879E-05
0.956596	0.499309317	2.58607E-05
0.957447	0.498518609	2.58336E-05
0.958298	0.497729206	2.58065E-05
0.959149	0.496941106	2.57794E-05
0.96	0.496154308	2.57523E-05
0.960851	0.495368808	2.57252E-05
0.961702	0.494584605	2.56981E-05
0.962553	0.493801696	2.5671E-05
0.963404	0.49302008	2.5644E-05
0.964255	0.492239753	2.56169E-05
0.965106	0.491460714	2.55899E-05
0.965957	0.49068296	2.55629E-05
0.966809	0.489906489	2.55359E-05
0.96766	0.489131299	2.55089E-05
0.968511	0.488357387	2.54819E-05
0.969362	0.487584752	2.5455E-05
0.970213	0.486813391	2.5428E-05
0.971064	0.486043302	2.54011E-05
0.971915	0.485274482	2.53741E-05
0.972766	0.484506931	2.53472E-05
0.973617	0.483740644	2.53203E-05
0.974468	0.48297562	2.52934E-05
0.975319	0.482211858	2.52665E-05
0.97617	0.481449354	2.52397E-05
0.977021	0.480688106	2.52128E-05
0.977872	0.479928113	2.5186E-05
0.978723	0.479169372	2.51591E-05
0.979574	0.478411881	2.51323E-05
0.980426	0.477655637	2.51055E-05
0.981277	0.476900639	2.50787E-05

0.982128	0.476146885	2.5052E-05
0.982979	0.475394372	2.50252E-05
0.98383	0.474643098	2.49984E-05
0.984681	0.473893061	2.49717E-05
0.985532	0.473144258	2.4945E-05
0.986383	0.472396689	2.49183E-05
0.987234	0.471650349	2.48916E-05
0.988085	0.470905238	2.48649E-05
0.988936	0.470161354	2.48382E-05
0.989787	0.469418693	2.48115E-05
0.990638	0.468677255	2.47849E-05
0.991489	0.467937036	2.47583E-05
0.99234	0.467198035	2.47316E-05
0.993191	0.466460249	2.4705E-05
0.994043	0.465723677	2.46784E-05
0.994894	0.464988316	2.46519E-05
0.995745	0.464254165	2.46253E-05
0.996596	0.463521221	2.45987E-05
0.997447	0.462789482	2.45722E-05
0.998298	0.462058945	2.45457E-05
0.999149	0.46132961	2.45192E-05
1	0.460601473	2.44927E-05