CERTIFICATION OF APPROVAL

Simulation of Sorption-enhanced Steam Reforming of Methanol for Hydrogen Production

by

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Approved by,

………………………….
(Assoc. Prof. Dr. Ye Lwin)

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TRONOH, PERAK
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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.

MOHAMAD HUSAINI BIN ABU BAKAR

ABSTRACT

This document reports on the study and research on the final year project entitled: Simulation of sorption-enhanced steam reforming of methanol for hydrogen production. The purpose of this simulation project is to study on the effects of different isothermal temperature and different S/M molar feed ratio towards maximizing hydrogen, H_2 and minimizing Carbon monoxide, CO concentration in presence of Carbon dioxide, CO_2 removal reaction. Currently, the steam reforming of methanol produced CO as byproduct. While, presence of CO in reformate gas can be poisonous towards cell electrode of Proton exchange membrane (PEM). Furthermore, high purity of H_2 produced will increase the fuel cell's durability and efficiency. In this study, the adsorption rate of CO_2 has been taken into consideration. Three main reactions is being study under this project together with CO_2 removal reaction mechanism. The Peppley kinetic reaction model has been choose to running this simulation and getting the final results. This project heavily involved in using mathematical software which is MATLAB$^{TM.}$ The results shows that at high temperature and high molar feed rate ratio (S/M) more hydrogen, H_2 is produced and reduction in CO concentration. The presence of CO_2 removal reaction significantly increases the purity of H_2 and reduced the amount of CO the zero level. Therefore, more study is required for better understanding in order to achieve an optimum production of H_2 for PEM reactor.

ACKNOWLEDGEMENT

First of all, praise to Allah S.W.T. the almighty who gave me the strength to face challenges in completing my final year research project.

Furthermore and the most importantly, I would to sincerely thank and deep appreciation towards my final year project supervisor, AP Dr. Ye Lwin for his constant supervision and continuous guidance in helping me in completing this final year project. Without his guidance, it would be very hard for me to complete the project within the allocated time.

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Lastly, I would like to thanks all parties who were involved directly or indirectly in completing my research study on Simulation on Sorption-enhanced steam methanol reforming for hydrogen production. All the contributions are highly appreciated.

Hopefully this project will bring benefits to all and can be used as reference at future time.

Thank you.

Table of Contents

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Recently, fuel cell technology that is one of the most promising sources of power regeneration offers a highly efficient conversion of chemical energy into electrical energy without emission of environment pollutants. (Appleby AJ, 1989) While, one of the fuels that mostly used in fuel cells system is hydrogen, H_2 or hydrogen-rich feed gas. Therefore, the interest in hydrogen production for fuel cells has increase.

In addition, the possibility of using an on-board methanol-steam reformer to generate H_2 for a fuel cell engine in various transportation applications such as cars has resulted in an increased interest in the study of the methanol-steam reforming process. One example of fuel cell that is being study is the low temperature proton exchange membrane (PEM). (Peppley, 1999)

Currently there are only a few fuel candidates that can be used in reforming produce H_2 on-board. Four of the best candidates are methanol, ethanol, gasoline and diesel. Methanol, CH_3OH is the most favorable candidates due to its characteristic. The comparison of these fuels concerning their application for reforming process has been performed in the work of *Lindstrom and Petterson.* (B. Lindstrom, 2001)

In methanol-steam reforming for production of H_2, there are three main reaction involved which is methanol-steam reforming, water gas shift (WGS) and methanol decomposition. There are some constraints for reforming and water gas shift (WGS) reaction because both are equilibrium limited and it is impossible to achieve complete conversion of CH_3OH to H_2 in single reactor under normal reaction normal condition. Therefore, the sorption-enhanced is introduced into the process. The sorption-enhanced process will remove the carbon monoxide, CO formed. Thus, a complete conversion of CH_3OH to H_2 can be achieved. (Peppley, 1999)

In addition, methanol-steam reforming process has a drawback where CO is being produced as a byproduct. Presence of CO can be hazardous towards performance of fuel cell. This is because CO can be poison towards fuel cell electrode. Report on effects of CO towards fuel cell performance can be study from the work of *N. Kurusawa, M. Hayashida, Y. Kamiya, H. Roppongi, D. Kurashima, and K. Wakayabashi.* (N. Kurusawa, 2003)

There are few criteria that can be checked to show the performance of sorption-enhanced steam reforming of methanol. One of the criteria is the ratio of H_2 to CO produced from the reaction. This ratio is targeted to achieve as high as possible in order to produce more H_2 and less CO. The factors that contribute towards the ratio value are through variation of reaction temperature and feed ratio of water, H_2O to methanol, CH_3OH.

1.2 PROBLEM STATEMENT

In order to produce H_2 as a fuel to fuel cell that drive the vehicles, mostly type of process applied is steam reforming of methanol. The steam reforming process with addition of Copper-based catalyst involved with three main reactions. Those reactions were methanol-steam reforming, water gas shift reaction and methanol decomposition.

Even though this type of process produces high quality of H_2, it also produces byproduct which CO. This CO is very dangerous and poisonous towards fuel cell electrode. In methanol-steam reforming process, the amount of CO that produced in dry product stream is at least 50 times more than amount allowed in fuel cell applications. The allowed amount of CO in fuel cell is less than 20 ppm. (H. Purnama, 2004)

Therefore, the product from methanol-steam reforming will need an extent process of purification. The H_2 purification process involved with CO removal method or simply reducing CO concentration. The CO concentration can be reduced by adding a cleanup step after the reforming process. The water gas shift reaction and the preferential oxidation reaction are considered as the most viable clean up processes available today for automotive fuel cell applications. (Li Y, 2000)

However, these processes are too complicated in size to practically meet the need of highly space-compact devices such as on-board generation of pure H_2 for a mobile fuel cell. (Caixia qi, 2009)

In addition, other purification method involved is catalytic CO oxidation in the presence of H_2. However, this purification method involved two simultaneous catalytic reactions which is CO and H_2 oxidation. Therefore, the catalyst must be highly active and selective toward CO oxidation in the presence of H_2. (P.V. Snytnikov, 2005)

For water gas shift reaction, where Carbon dioxide, CO_2 is removed the reaction of CO_2 adsorption must be done in simultaneously. This is because to reduce the capital cost reduction through a simplification process. Besides that, it also improved on the energy efficiency for the process.

Finally, it is essential to produce a high purity of H_2. This is because of higher purity of H_2 in fuel cell will brings higher durability and increase the efficiency of the fuel cell.

1.3 OBJECTIVES

i. To demonstrate by simulation of CO_2 adsorption in order to reduce CO and produce more Hydrogen, H_2.

ii. To study the effects of different properties of :

    a) Steam/Methanol ratio

    b) Reactor temperature

    c) Presence of CO_2 removal

in order to show on the yield and purity Hydrogen,H_2 produced.

iii. To study the concentration profile and adsorption rate profile of sorption-enhanced steam reforming at different isothermal temperature and Steam/Methanol molar feed ratios.

1.4 SCOPE OF STUDY

This project is concerns on the effects of different feed ratios, different reaction temperatures on production of H_2 and the presence of CO adsorbent in reaction mechanism. In order to analyze the H_2 production which is targeted to produce high concentration of H_2 and low concentration of CO, a few criteria has been taken into consideration. Those criteria involved are isothermal temperature, feed ratio and types of sorbent used.

Furthermore, this project also involved understanding the interactions of reactions involved in methanol-steam reforming. There are three main reactions involved which are methanol-steam reforming, water gas shift reaction (WGS) and methanol decomposition.

The adsorption is being taken into consideration in addition to the three main reactions above as to check the effectiveness of CO_2 removal on the steam reforming process. Besides that, the effects of using different sorbent in the reaction can be analyzed through adsorption rate of CO_2 removal.

1.4.1 Relevancy of the project

The purpose of this project is to demonstrate by simulation, the sorption-enhanced steam reforming by methanol in order to produce high purity H_2 and lower concentration of CO. Currently, there are numerous numbers of researches and studies done related to sorption-enhanced steam reforming in hydrogen production. Those research mostly involved with study of different sorbent and catalyst used at different conditions in sorption-enhanced steam reforming process using various kinetic models.

While, this project is to study on the effects of high temperature and different feed ratio in sorption-enhanced steam reforming using one type of kinetic model. In addition, the effects of two types of sorbents were also being studied.

Besides that, most of the computational studies that have been done on sorption-enhanced steam reforming are based on the reaction dynamics. There are almost none regarding the kinetic simulation study on this. Thus, this project is highly relevant and timely.

1.4.2 Feasibility of project within the scope and time frame

The first phase of the project (FYP1) involved with collecting and study any materials related to the methanol-steam reforming process in hydrogen production. Such related materials were journals, related website, reference books and through discussion with supervisor. It is expected that at the end of first phase of the project (FYP1), the writer will have a full understanding of the theory, mechanism and process involved related to this project.

Meanwhile, second phase of the project (FYP2), the writer will focus on performing the simulation related to this project. It is expected at the end of FYP2, the writer will complete his simulation and being able to produce a final report on this project. Thus, the writer’s final year project will be completed.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION TO SORPTION-ENHANCED STEAM REFORMING

In SERP, the hydrogen production and CO_2 removal are combined in one step. Industrial hydrogen is produced in reformer both in steam-methane reforming (SMR) of methane and water-gas shift (WGS) reaction. This reaction is important in producing hydrogen. The reactions involved are:

i. Steam-methane reforming (SMR) reactions :

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad (\Delta H_{298}{}^0 = +206 \text{ kJ/mol}) \qquad (1)$$

ii. Water-gas shift (WGS) reaction :

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (\Delta H_{298}{}^0 = -41 \text{ kJ/mol}) \qquad (2)$$

In sorption-enhanced steam-methane reaction, a suitable sorbent is mixed with SMR catalyst. The function of that sorbent is to remove CO_2 that produced in the reactions. Thus, the reaction equillibria will shift towards product side of the SMR and WGS reaction. Thus, CO_2 removal or capture processes must be combined in single step to achieve this effect. The same CH_4 conversion may be obtained at much lower temperatures, say between 723 K and 823 K, than in conventional SMR without sorbent which is performed typically between 1123 K and 1223 K. (Hendricus Th. J. Reijers, 2009)

In addition, the sorbent used must be able to remove CO_2 at high temperature. Sorbents like amine solutions, physical solvents, active carbons and zeolites are able to remove CO_2 at temperature below 373 K and become constraint at higher temperature. The suitable or mostly used sorbents is metal oxides, hydrotalcites, lithium metal oxides, and double salts. All of sorbents is suitable because they can absorb CO_2 at high temperature used for steam reforming reactions. (Reijers, 2006)

Besides that, the sorbent may be mixed with a WGS catalyst in a separate reactor downstream of the steam-methane reformer where all reactions except for the SMR reaction to be combined in one reactor. (Allam, 2005)

However, the advantage of the second option compared from the first option is that it is much easier to complete the WGS reaction by SERP than SMR reaction. This requires the sorbent to being able to absorb down to a very low CO_2 concentration in order to obtain higher CH_4 conversion. (Cobden, 2007)

Later, the CO_2 concentration will be reduced to 270 ppm at 1 bar and to 10 ppb at 17 bars in order to obtain 90% CH_4 conversion at 673 K. For any system that provided with SERP, it should have a regeneration step to remove the adsorb CO_2. This is because the sorbent will saturated after some time with CO_2. Therefore, it is advisable to have a batch process where the reactor periodically subject to series of steps at different conditions for the desired processes such as sorption-enhanced reaction, depressurization, steam purge and repressurization. (Waldron, 2001)

2.2 DIFFERENT METHODS OF CO REMOVAL

As mention on the above section, the SERP will produce a significant amount of CO concentration in feed gas (H_2) to the fuel cell. The present of CO in feed gas is very dangerous and can be poisonous to the platinum catalyst on the anode inside the fuel cell. It is reported that CO has detrimental effects on the performance of the fuel cell at concentration above 50 ppm. (Rohland B, 1999)

Unfortunately, the hydrogen produced by steam reforming of methanol contains a significant amount of CO (<100 ppm) as a by-product formed during the reaction. However the CO concentration can be reduced by adding a cleanup step after the fuel processor. The water gas shift (WGS) reaction and the preferential oxidation reaction are considered as the most viable clean up processes available today. (Caixia qi, 2009) But other method of CO removal will also be discussed.

2.2.1 Preferential oxidation (PROX)

PROX is a catalytic process in which a small amount of O_2 is added to selectivity oxidizes CO in preference to H_2. The final product from this purification option is typically consists of 95% of H_2 with only trace concentration of CO. (Harrison, 2008) The reaction involved in PROX reaction is:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad (\Delta H^0 = -241.1 \text{ kJ/mol}, \Delta G^0 = -228.6 \text{ kJ/mol}) \qquad (3)$$

2.2.2 Water gas shift (WGS) reaction

The water gas shift reactor which is significantly reduces the CO concentration downstream of the reformer, is the critical component of the fuel processor. $Cu/ZnO/Al_2O_3$ commercial catalyst has long been used in the water gas shift reaction. Although the results have been positive, it is very difficult to achieve CO level below 10 ppm with these catalysts.

In addition, the catalyst is pyrophoric and consequently degrades during operation particularly when exposed to air. The water gas shift reactor is often the largest component of the fuel processor and its performance is based on the activity of the catalyst. (Elise S. Bickfor, 2004) The reaction that involved in water gas shift reaction is:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (\Delta H^0 = 41.1 \text{ kJ/mol}, \Delta G^{o} = -28.6 \text{ kJ/mol}) \qquad (4)$$

2.2.3 Oxygen-assisted water gas shift (WGS) reaction (OWGS)

This type of CO removal method consists of two combined method of PROX and WGS reaction. The oxygen is incorporated into the process to facilitate the WGS reaction over the new catalyst to reach low CO outlet concentration. (Elise S. Bickfor, 2004) The reaction involved is:

$$(1 + x)CO + H_2O + {}^{x}/_{2}\, O_2 \rightarrow (1 + x)CO_2 + H_2 \qquad (5)$$

2.2.4 Catalytic CO oxidation in the presence of H_2

This purification technique involved two simultaneous catalytic reactions which is CO oxidation and H_2 oxidation. Therefore, an efficient catalyst for the reaction must be both highly active and selective toward CO oxidation in the presence of H_2.

Numerous supported metal catalyst have been suggested for this method including active and selective Pt- and Ru- containing catalyst supported on γ-Al_2O_3 and carbon materials. Besides that, it is vital to enhance the activity of these catalysts and to reduce their noble metal content. A way of solving this problem is by employing bimetallic catalysts and metal catalysts promoted with metal oxides.

2.3 TYPE OF ADSORBENT – HYDROTALCITE-LIKE COMPOUNDS(HTLCS)

In the process of removal CO_2, the most important issues are to find the right adsorbent for the process. There are few criteria of adsorbent that need to be taken into consideration, whereas the adsorbent must have (Zou Young, 2001):

i. High selectivity and adsorption capacity for CO_2 at high temperature.

ii. An adequate adsorption/desorption kinetics for CO_2 under operating conditions.

iii. Stable adsorption capacity for CO_2 after repeated adsorption/desorption cycles.

iv. An adequate mechanical strength of adsorbent particles after cyclic exposure to high pressure streams.

Based on the criteria above, hydrotalcite like compounds (HTIcs) have met all the requirements above and suitable for CO_2 sorption process.

Hydrotalcite like compounds (HTIcs) belong to a large class of anionic and basic clays or also known as layered double hydroxides (LDH). LDH composed of positively charged brucite-like, $Mg(OH)_2$, layers with trivalent cations substituting for divalent cations at the centers of octahedral sites of hydroxide sheets. This hydroxide sheets where vertexes contain hydroxide ions and each –OH group is shared by three octahedral cations and points towards the interlayer regions.

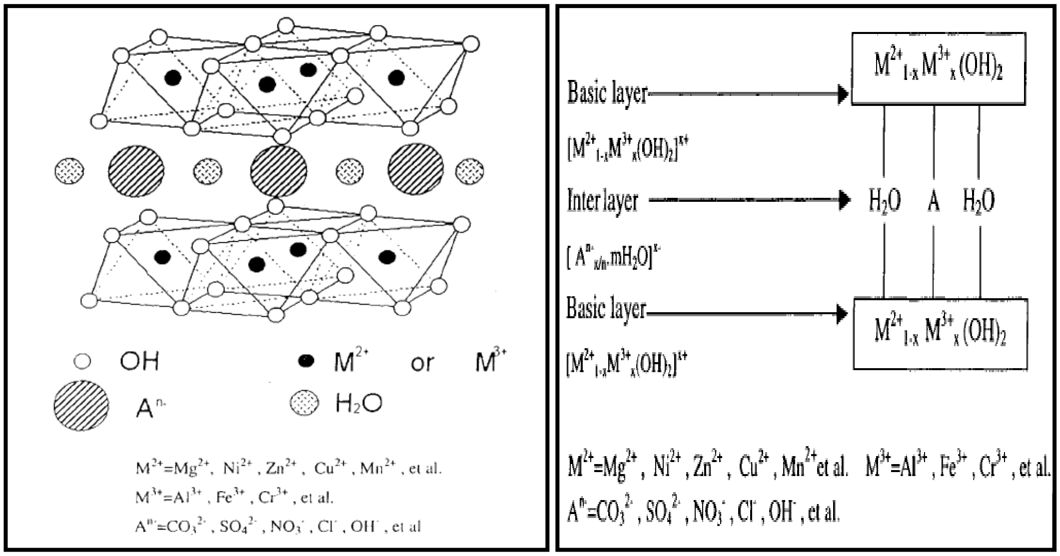
The excess positive charge of HTIcs is compensated for by anions and water molecules present in the interstitial positions which can be represented by the general formula.

$[(M^{2+}{}_{1-x}\,M^{3+}{}_{x}(OH)^{2}\,)^{x+} \bullet (A^{n-}{}_{x/n} \bullet mH_2O)^{x-}\,]$ (6)

Where $M^{2+} = Mg^{2+}$, Ni^{2+} , Zn^{2+} , Cu^{2+}, or Mn^{2+} ; $M^{3+} = Al^{3+}$, Fe^{3+} , or Cr^{3+};

$A^{n-} = CO_3{}^{2-}$, $SO_4{}^{2-}$, NO^{3-}, Cl^{-}, or OH^{-} and X is normally between 0.17 and 0.33 but there is no limitation.

However, HTlcs is yet to receive a considerable attention in recent years because they are used in a wide range of applications like's catalysts, precursors and supports of catalyst; ion exchangers; filters; decolorizing agents; industrial adsorbents; polymer stabilizer; optical hosts and ceramic precursors. Besides that only a few paper that reports on HTlcs as an adsorbents for CO_2.



Structure models for Hydrotalcite-like compounds $[(M^{2+}{}_{1-x}\ M^{3+}{}_{x}(OH)^{2})^{x+} \bullet (A^{n-}{}_{x/n} \bullet {}_{m}H_2O)^{x-}]$ (HTlcs), 3-D structure and 2-D structure.

2.4 CO_2 SORPTION ON HYDROTALCITE-LIKE COMPOUNDS(HTIcs)

A lot of research has been done in order to find the right and most suitable adsorbent to be used in removing CO_2 during SMR. In one of the research, it was report that hydrotalcite like compounds (HTIcs) have met all the requirements for the absorbents and could be fit in sorption-enhanced reaction process (SERP). (Hufton, 2001) (Ding Y, 2000) Besides that, reported in Hufton et al. (Hufton. J, 1999) , a 25-30% cost reduction due to use of hydrotalcite (HTIcs) after comparing with cost by using conventional methane-steam reforming.

In the work of *Zou Yong, Vera Mata, and Alirio E. Rodrigues* (Zou Young, 2001) , two types of commercial hydrotalcite-like compounds were studied as adsorbents for CO_2 at elevated temperatures. All the sample have an adsorption capacity for CO_2 higher than 0.30 mmol/g at 300^0C and 1 bar, which meets the requirements for the sorption-enhanced reaction process.

HTIcs can be directly used as adsorbents for the removal and recovery of CO_2 from power plant fuel gases. The HTIcs containing CO_3^{2-} show higher adsorption capacities than those containing OH^-. The presence of low water content in the HTIcs is favorable for the adsorption of CO_2. The aluminum content in substituted HTIcs and the heat treatment temperature strongly affect the adsorption capacity and there is an optimum aluminum content and heat treatment temperature when HTIcs are used as adsorbents for CO_2 at elevated temperatures.

2.5 KINETIC MODELING OF METHANOL-STEAM REFORMING

For the production of hydrogen and CO in fuel cells, a kinetic model of methanol-steam reforming is very important. This kinetic model is not only able to predict the rate of production of hydrogen but also rate of production of undesired product CO. For the past decades, al lot of study and research has been done particularly on kinetic studies on process occurs on $Cu/ZnO/Al_2O_3$ catalysts during methanol synthesis.

However, there are less numbers of researches published concerning the water gas shift (WGS) reaction on $Cu/ZnO/Al_2O_3$ but there is a debate over whether the mechanism is associative via an intermediate formate or regenerative via a redox reaction involving a special form of Copper. By contrast, the literature to date on methanol-steam reforming is relatively limited and only a few studies have attempted to develop kinetic models based on surface reaction mechanism.

2.5.1 Water gas shift (WGS) reaction on $Cu/ZnO/Al_2O_3$

There has been a debate on the exact nature of the surface mechanism for the water gas shift reaction on $Cu/ZnO/Al_2O_3$ catalyst for the past decades. The main issues are whether the reaction proceeds via an associative mechanism or a regenerative mechanism. In the associative mechanism, H_2O and CO reacts to form an adsorbed intermediate surface formate which then decomposes to form H_2 and CO_2. In the regenerative mechanism, also known as the redox mechanism, Copper oxide reacts with CO to form CO_2 and Copper metal. Water then dissociates to produce H_2 and surface oxygen which re-oxidizes the Copper.

Rhodes .et.al. (C. rhodes, 1995) concluded that both regenerative and associative mechanism may be occurring at comparable rates for some catalyst conditions, while certain catalyst-conditioning treatments may cause one or the other of the mechanism to dominate.

While, *Dumpelmann*, in his investigation of methanol-steam reforming on a $Cu/ZnO/Al_2O_3$ catalyst, proposed an associative mechanism for the water gas shift reaction which proceed through an intermediate formate. *Duempelmann* (Empelmann, 1992) found this mechanism agreed with his observation of the kinetics of the water gas shift mechanism under typical operating conditions for methanol-steam reforming.

2.5.2 Methanol-steam reforming

In *Santacesaria* and *Carra* work, they have published a paper which used an empirical approach to develop an expression for the rate of disappearance of methanol. (E. Santacessaria, 1981) Their rate expression was of the form of a Langmuir-Hinshelwood expression but it was not derived from an explicit mechanism. While *Amplett et. Al.* (J.C. Amphlett, 1988) reported studies of both the thermodynamics and the kinetic of methanol-steam reforming on $Cu/ZnO/Al_2O_3$ catalysts.

Furthermore, the kinetic expression developed by *Jiang et al.* predicts the rate of disappearance of methanol and the rate of formation of CO_2. (J.Jiang, 1993)They claim that the process is 100% selective for CO_2 and that rate of the WGS reaction is negligible.

Although for industrial processes the rate of CO production could be considered negligible, for low temperature fuel-cell applications where very low levels of CO contamination can severely poison the anode electrocalatalyst, the decomposition reaction and the WGS must be taken into account.

Despite the simplification used by *Jiang et al.* the surface mechanism which they propose provides the best explanation for the observed kinetic behavior and also accounts for the high rate of methyl formate production which occurs when the S/M ratio is low.

CHAPTER 3

METHODOLOGY

3.1 RESEARCH METHODOLOGY

In order to study the performance of adsorbent at different temperatures and feed ratios, a kinetic equation for sorption as a function of CO_2 partial pressure and temperature has been taken from the comprehensive kinetic model of *Peppley et al.* This model composed of kinetic expressions of steam-methanol reforming, methanol decomposition and water gas shift reaction (WGS).

This *Peppley et al.* model is complex it is represent the composition profiles of the reactor for wide ranges of temperature and steam-methanol ratios. $^{\text{(Ye Lwin)}}$ The *Peppley et al.* model shown below:

$$r_{SR} = S_A \frac{k_{SR}\ K^*_{CH3O^{(1)}}\left({P_M}/{\sqrt{P_H}}\right)\left(1-P_H^3 P_C/K_{SR}P_M P_W\right)C_{S1}^T C_{S1a}^T}{\left(1+K^*_{CH3O^{(1)}}\left(P_M/\sqrt{P_H}\right)+K^*_{HCOO}P_C\sqrt{P_H}+K^*_{OH^{(1)}}\left(P_W/\sqrt{P_H}\right)\right)\left(1+\sqrt{K_{H1A}P_H}\right)} \tag{7}$$

$$r_D = S_A \frac{k_D\ K^*_{CH3O^{(2)}}\left({P_M}/{\sqrt{P_H}}\right)\left(1-P_H^2 P_W/K_D P_M\right)C_{S2}^T C_{S2a}^T}{\left(1+K^*_{CH3O^{(2)}}\left(P_M/\sqrt{P_H}\right)+K^*_{OH^{(2)}}\left(P_W/\sqrt{P_H}\right)\right)\left(1+\sqrt{K_{H2A}P_H}\right)} \tag{8}$$

$$r_{WGS} = S_A \frac{k_{WGS}\ K^*_{OH^{(1)}}\left({P_M P_W}/{\sqrt{P_H}}\right)\left(1-P_H P_C/K_{WGS}P_N P_W\right){C_{S1}^T}^2}{\left(1+K^*_{CH3O^{(1)}}\left(P_M/\sqrt{P_H}\right)+K^*_{HCOO}P_C\sqrt{P_H}+K^*_{OH^{(1)}}\left(P_W/\sqrt{P_H}\right)\right)^2} \tag{9}$$

The expression for rate of CO_2 adsorption been taken from *Ding and Alpay et al.* by using linear driving force (LDF) model which has shown below:

$$r_{ADS} = \frac{dq_{CO2}}{dt} = K_{ADS}\,(q^*_{CO2} - q_{CO2}) \tag{10}$$

The expressions and value for the rate parameters in equation (7) – (9) were taken from *Peppley, et. Al.* While, the parameters for the expression of q^*_{CO2} were taken from *Ding and Alpay et al.* The rate equation for methanol-steam reforming is given below:

i. Steam reforming:

$$CH_3OH(g) + H_2O(g) \rightarrow CO_2(g) + 3H_2(g) \tag{11}$$

ii. Methanol decomposition:

$$CH_3OH(g) \rightarrow CO(g) + 2H_2(g) \tag{12}$$

iii. Water gas shift:

$$CO\ (g) + H_2O(g) \leftrightarrow CO_2(g) + H_2\ (g) \tag{13}$$

However, for the presence of CO_2 removal method, there is additional equation involved which is:

iv. CO_2

$$CO_2\ (g) + * \rightarrow CO_2^* \tag{14}$$

The steady state one-dimensional pseudo-homogeneous pug flow reactor model is been using for reactor simulation. The governing material balance equations for the six components are given below:

Space rate (profile) of conversion of species,i = (time rate of conversion,i) (space time) (15)

$\frac{dY}{dz} = \ , \left(\sum_j V_{ij} r_j\right) \frac{\rho_b A}{F_{io}}$, i = CH_3OH, H_2O, CO, CO_2, H_2 , CO_2^* (16)

With the initial conditions Yi = 0 at Z = 0 (entry to catalyst bed).

Where Yi = conversion of species i per mole of methanol fed

$$F_i \ = F_{io} + \ Y_i F_{MO} \tag{17}$$

$$P_i = \frac{F_i}{\sum F_i} P \tag{18}$$

Although the operations of adsorptive reactors are inherently transient because of the limitation of equilibrium capacity of the stationary adsorbent, a steady state operation equivalent to membrane reactors was assumed in order to simplify the calculations.

3.2 PROJECT ACTIVITIES

This project mostly involved with using MATLAB^{TM} simulation software whereas this project begin finding any information or material particularly on recent research or journal with regards to sorption-enhanced steam reforming of methanol. Then, the project progress continues with selecting the kinetic reaction and reactor simulation model. This will be the target at the end of FYP1. FYP2 begin with implementing the model chosen in the MATLAB^{TM} for simulation process. After getting all the results from the simulation, the results being synthesis and discuss.

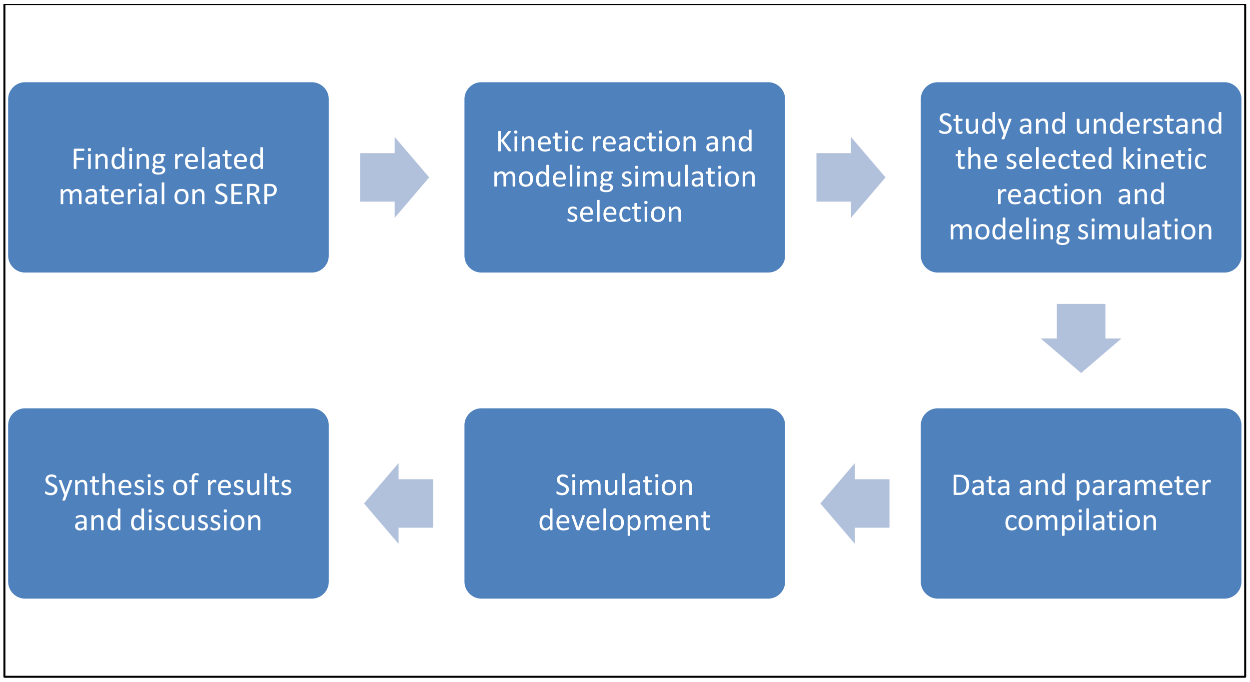


Figure 1 : Project process flow

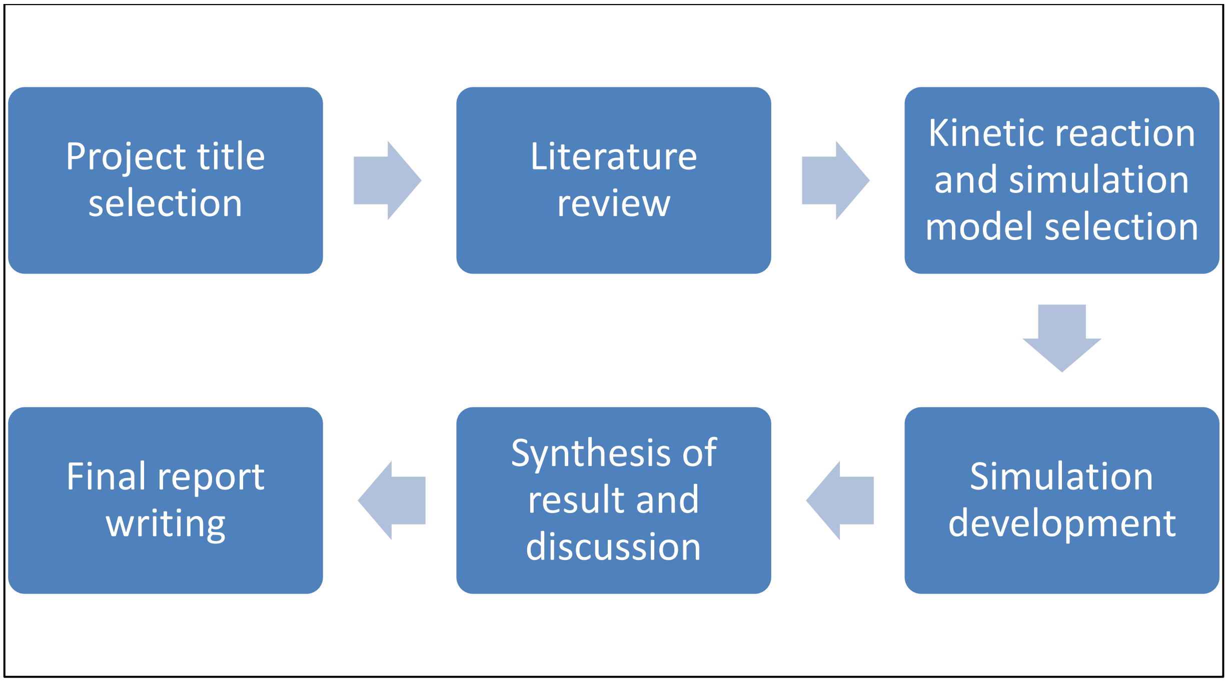


Figure 2 : General project activities

3.3 CALCULATION STEPS

The calculation steps involved for this simulation is consists of two cases. The first cases is running the simulation by including the CO_2 removal equation

i. Calculate F_i from Equation17 and assuming Conversion, Yi = 0. This is only applicable to Methanol and Steam (H_2O).

ii. Find initial partial pressure of Methanol and Steam(H_2O) from Equation 18.

iii. Substitute the calculated partial pressure of Methanol and Steam(H_2O) into the Peppley kinetic model.

iv. Rearrange the Peppley Kinetic Model (All the reaction involved in kinetic model is not divided by zero)

v. Apply the rearrange kinetic model into Equation 16.

vi. Solve the differential equation of Equation 16 by using MATHLAB.

    a. The propose solver is by using the ode23s.

    b. The conversion value Y_i is recorded.

    c. Use step size, Z = 0.05

vii. The conversion, Y_i obtained is substitute into Equation 17 to calculate F_i for each compound.

viii. Using Equation 18 to calculate the partial pressure of each compound.

ix. All the partial pressure calculated is substitute to the original Peppley kinetic model.

x. Solve Equation 16 in order to calculate the final conversion of each compound.

    a. Use MATHLAB function ode23s.

   b. Value of Z range is from 0 until 1.

   c. Defaults step size value is used.

xi. Used Equation 17 to calculate the final flow rate of each compounds. (Reactor outlet flowrate)

xii. Finally used Equation 18 to calculate partial pressure of each compounds.

xiii. Repeat the entire step starting from 1 until 11 with different reactor temperature and Steam/Methanol ratio.

The operating parameters of the reactor used for the simulation and the kinetic model are given in the table below:

Parameter	**Value**
Bed density, p_b	1500 kg m^{-3}
Surface area of catalyst, S_A	1.0E+5 m^2 kg^{-1}
Bed diameter, A	0.02 m
Bed voidage, ε	0.5
Bed length, L	0.1 m
Reaction temperature, T	473-673 K
Pressure, P	1.0 bar
Methanol feed rate, F_{MO}	2.0 mmol s^{-1}
Steam/Methanol molar feed ratio	1,2,3
Inert (nitrogen) flow rate	2.0 mmol s^{-1}

Table 1 : Operating parameter

CHAPTER 4

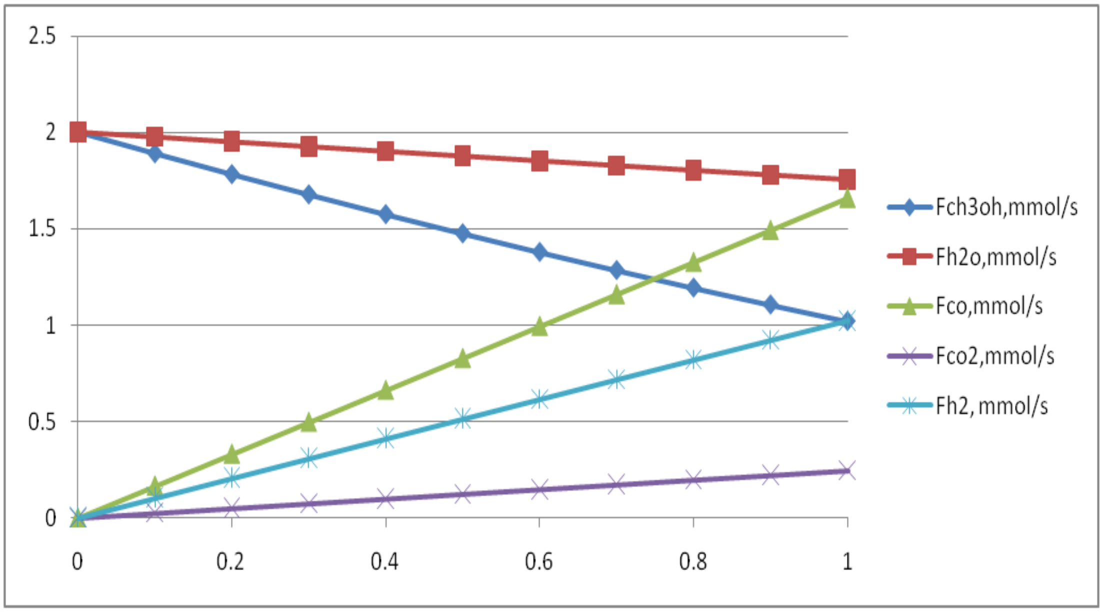
RESULTS AND DISCUSSION

4.1 CASE 1 : METHANOL STEAM REFORMING WITHOUT CO_2 REMOVAL.

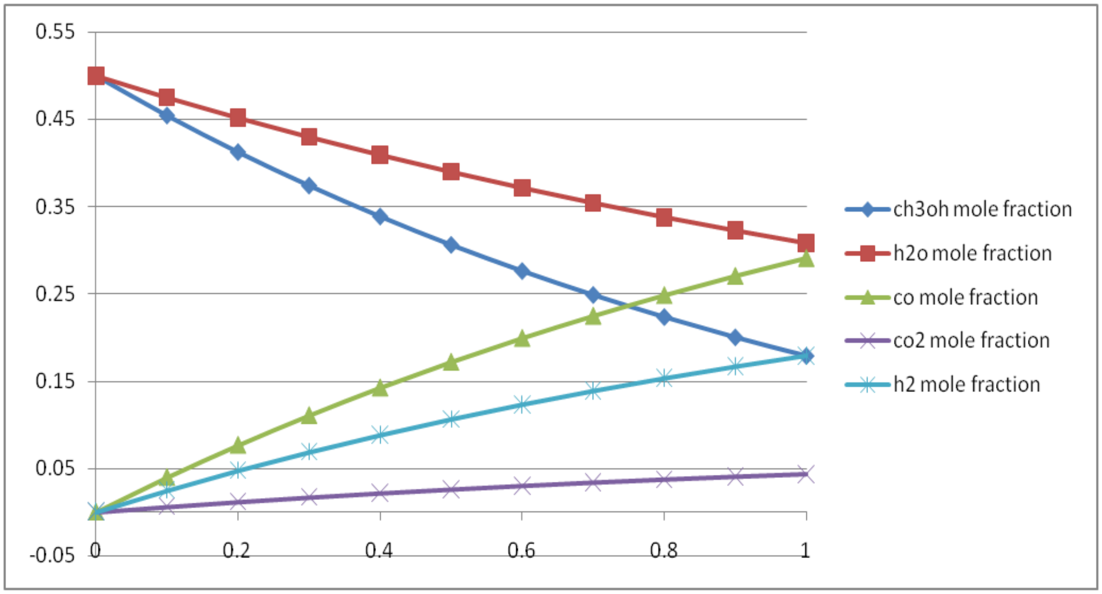
4.1.1 Methanol steam reforming with S/M = 1

i. At T = 473 K

a. Flow rate

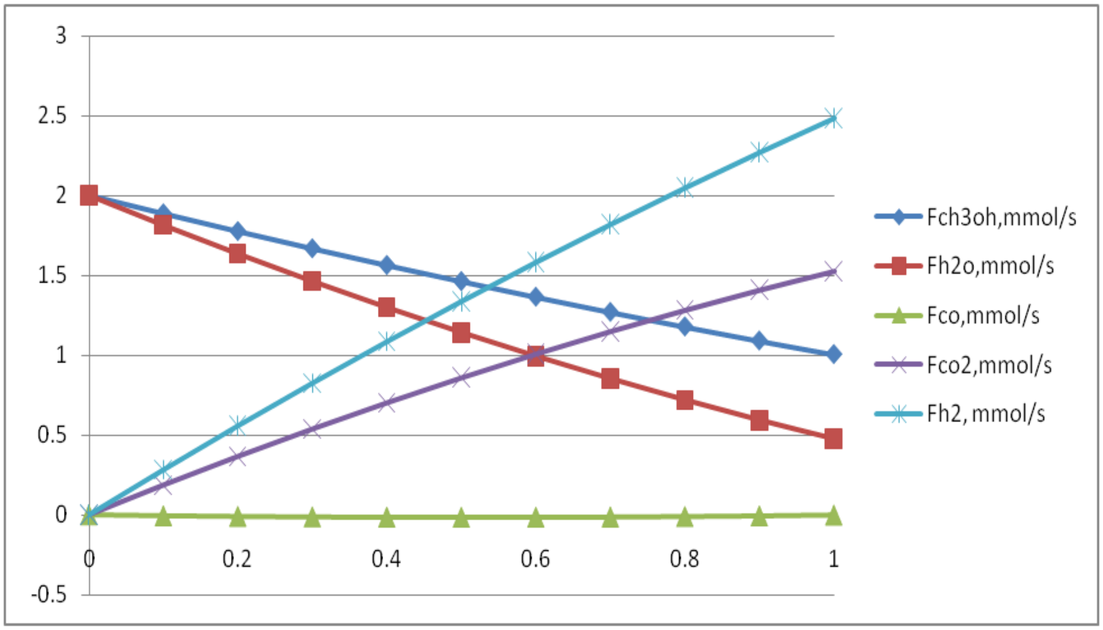


b. Mole fraction

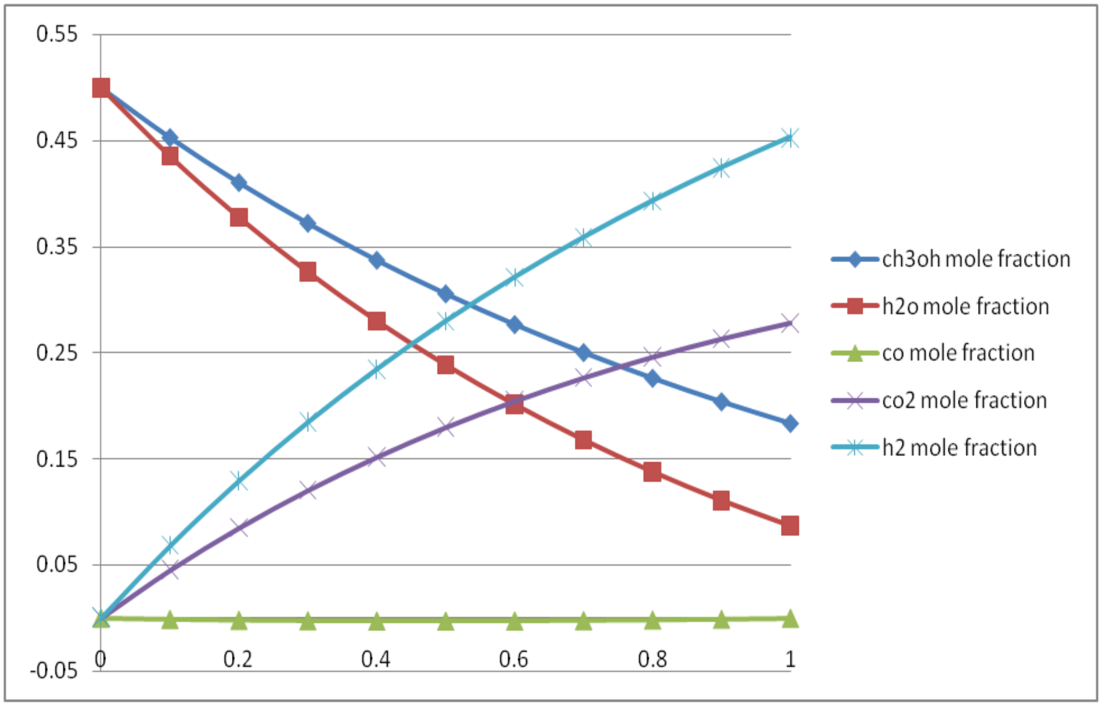


ii. At T = 573 K

a. Flow rate

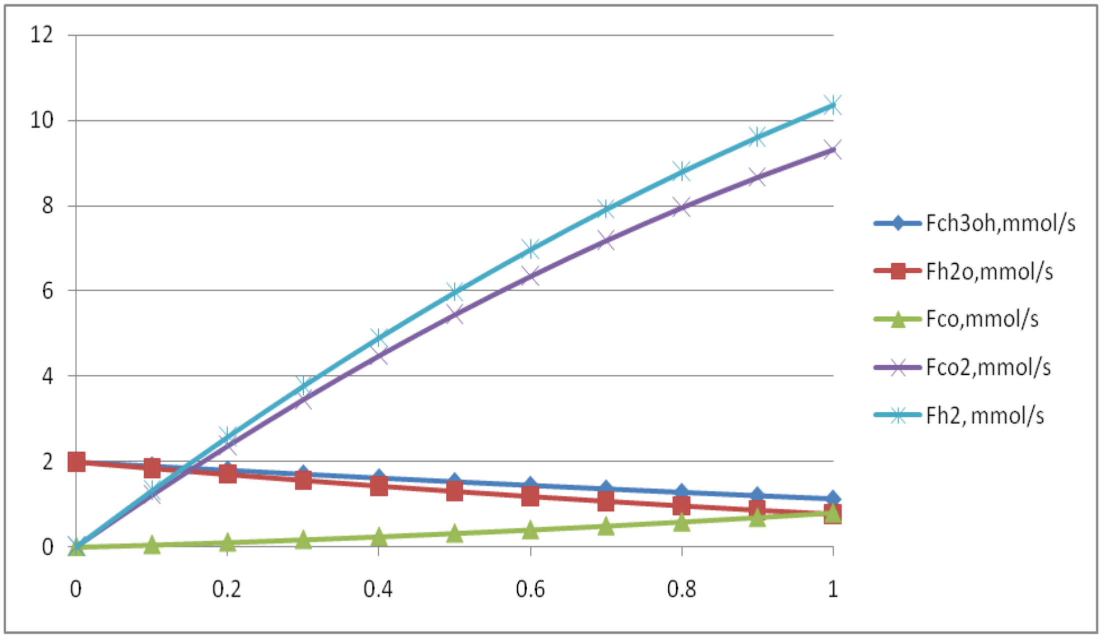


b. Mole fraction

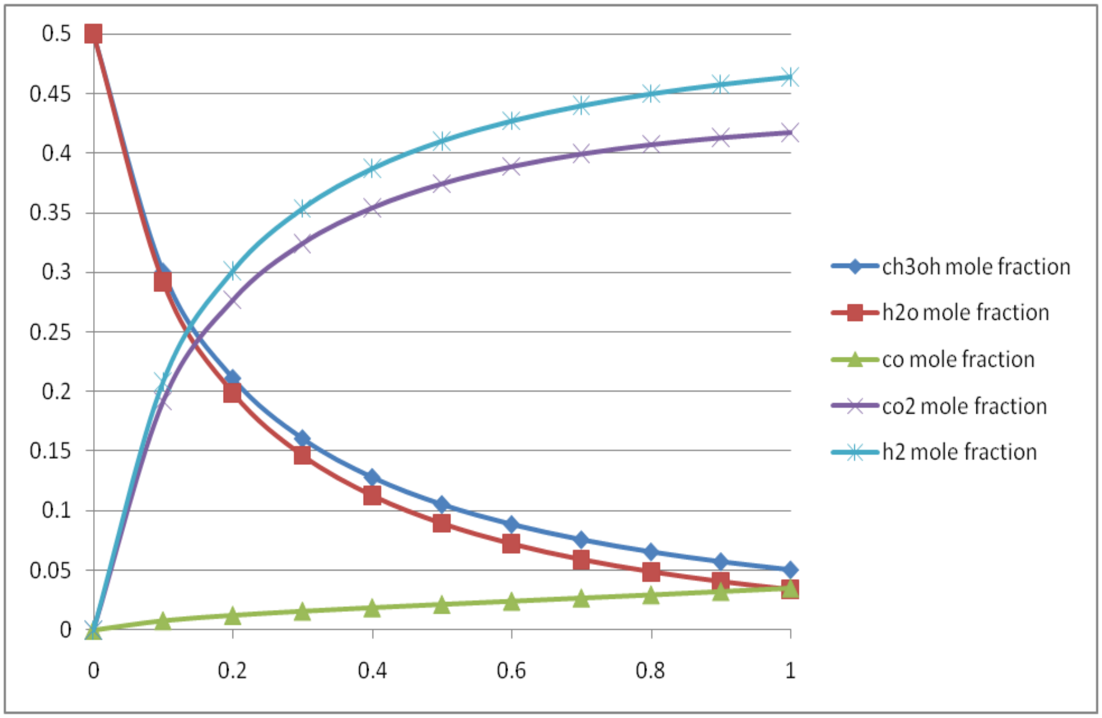


iii. At T = 673 K

a. Flow rate



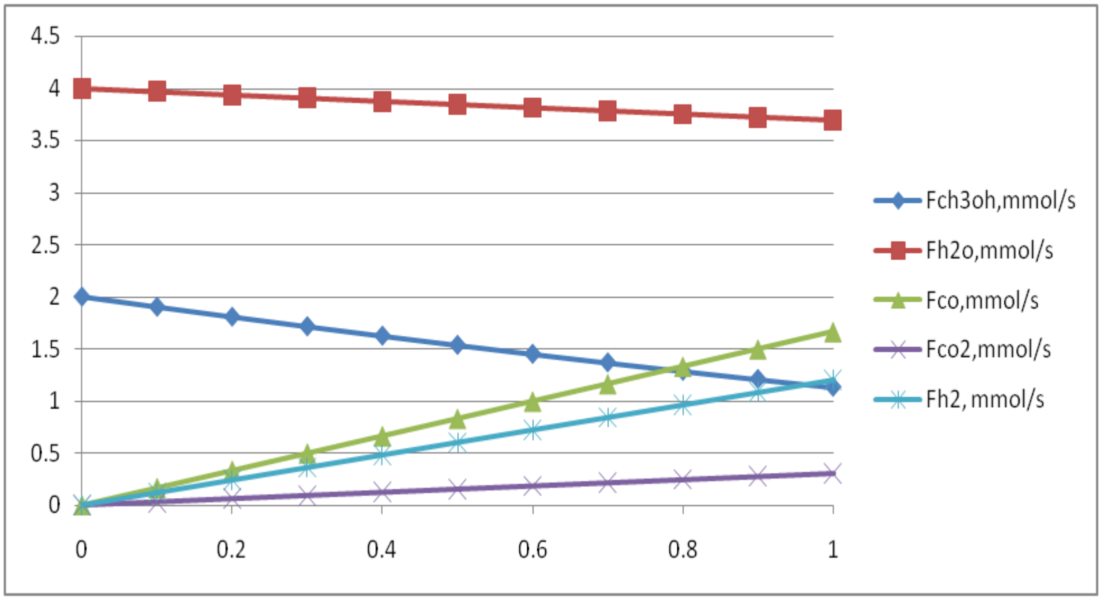
b. Mole fraction



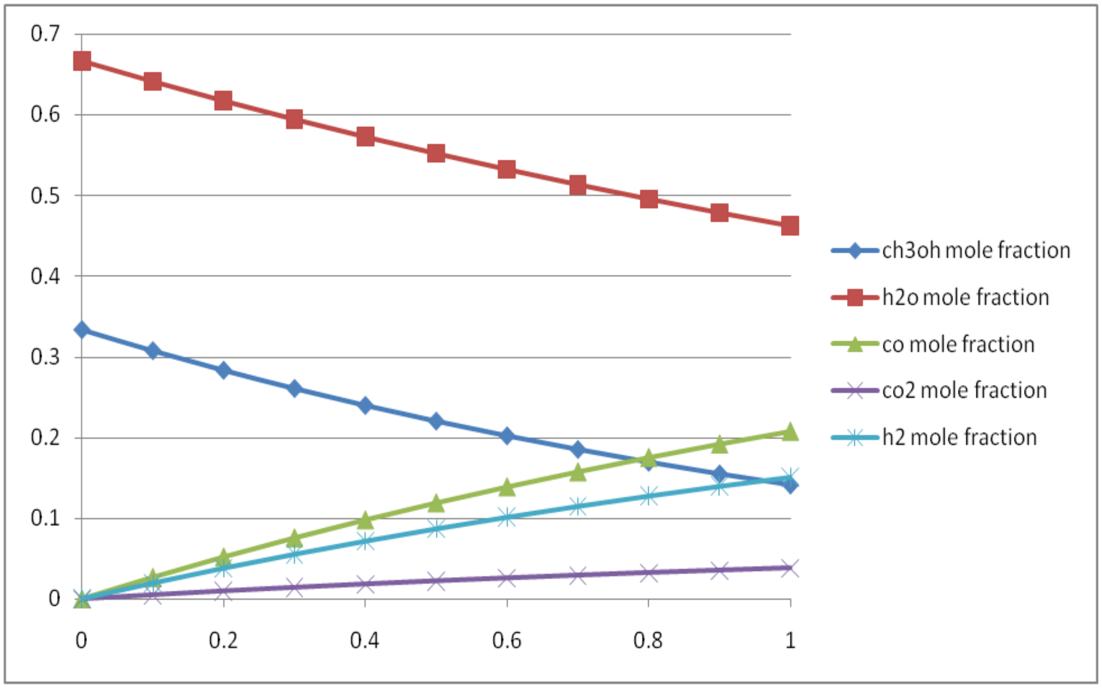
4.1.2 Methanol steam reforming with S/M = 2

i. At T = 473 K

a. Flow rate

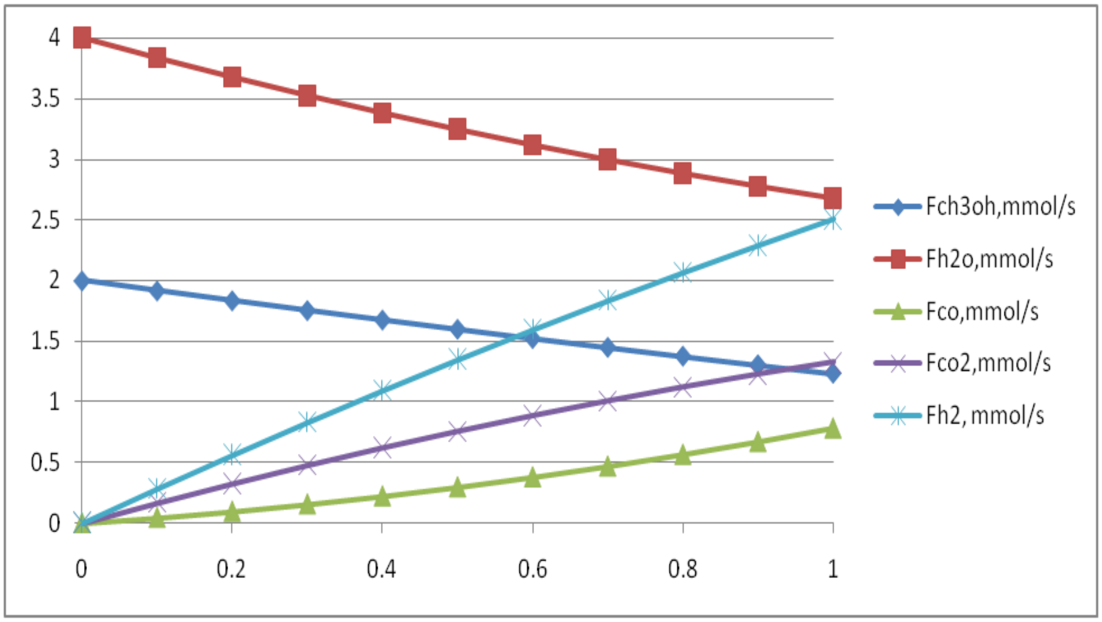


b. Mole fraction

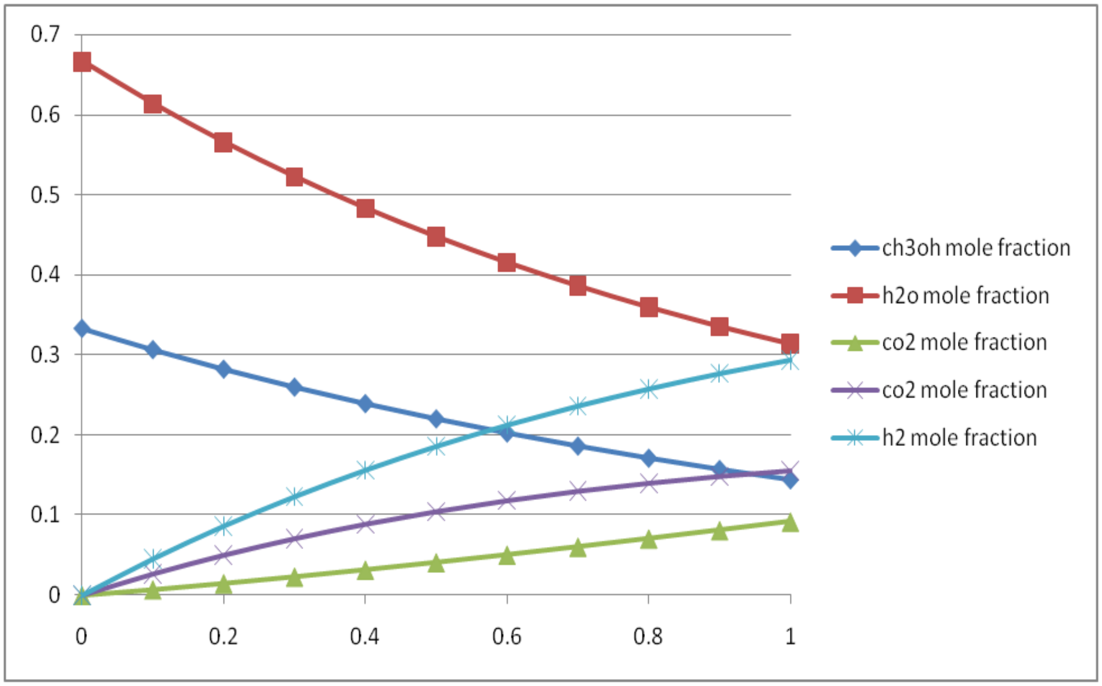


ii. At T = 573 K

a. Flow rate

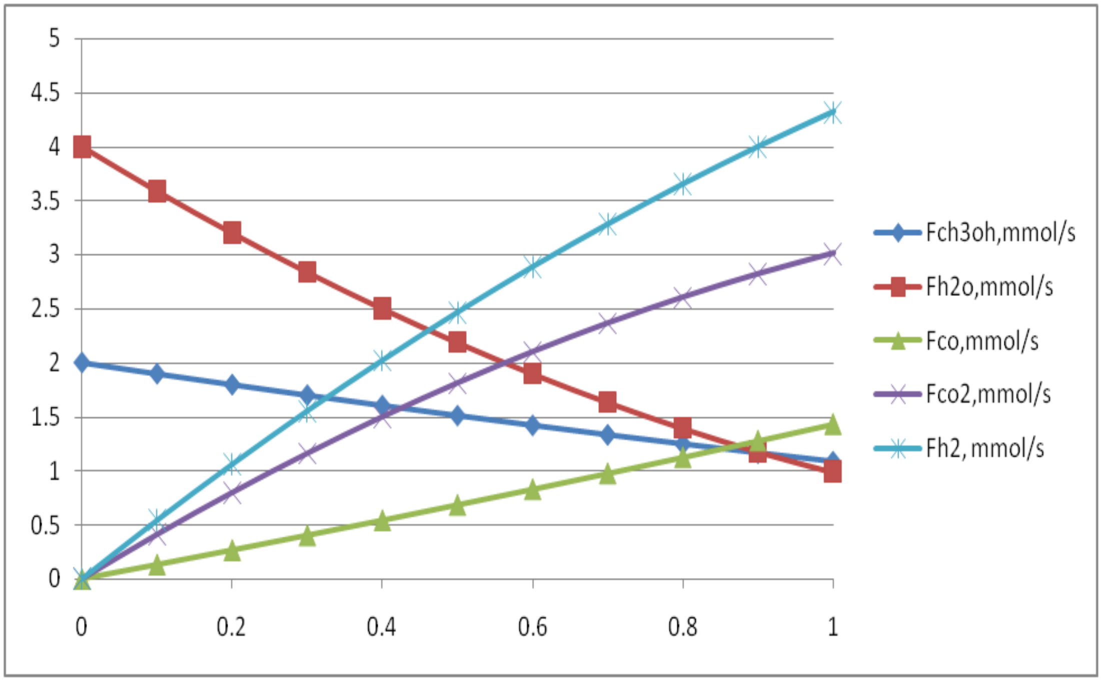


b. Mole fraction

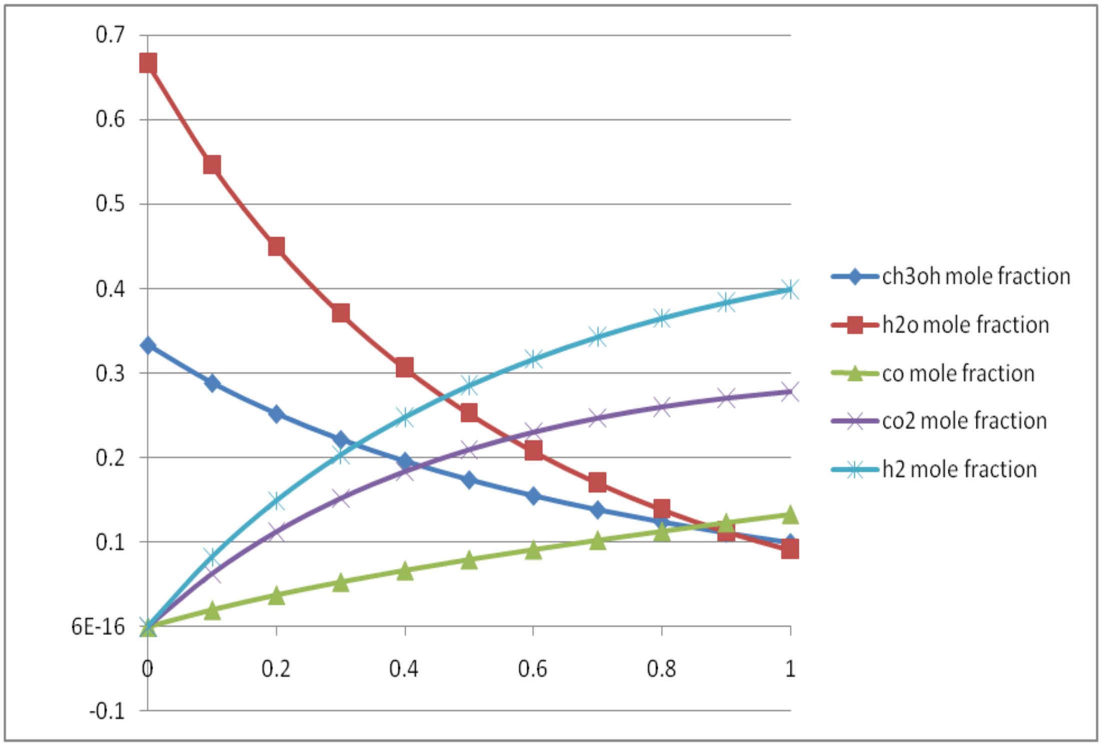


iii. At T = 673 K

a. Flow rate



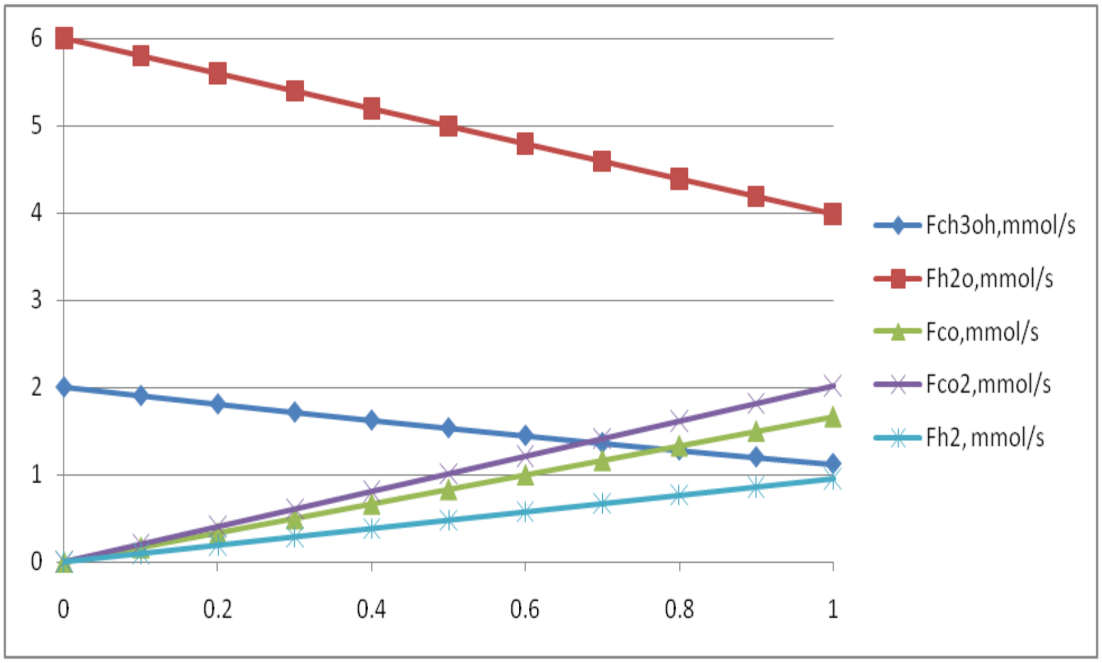
b. Mole fraction



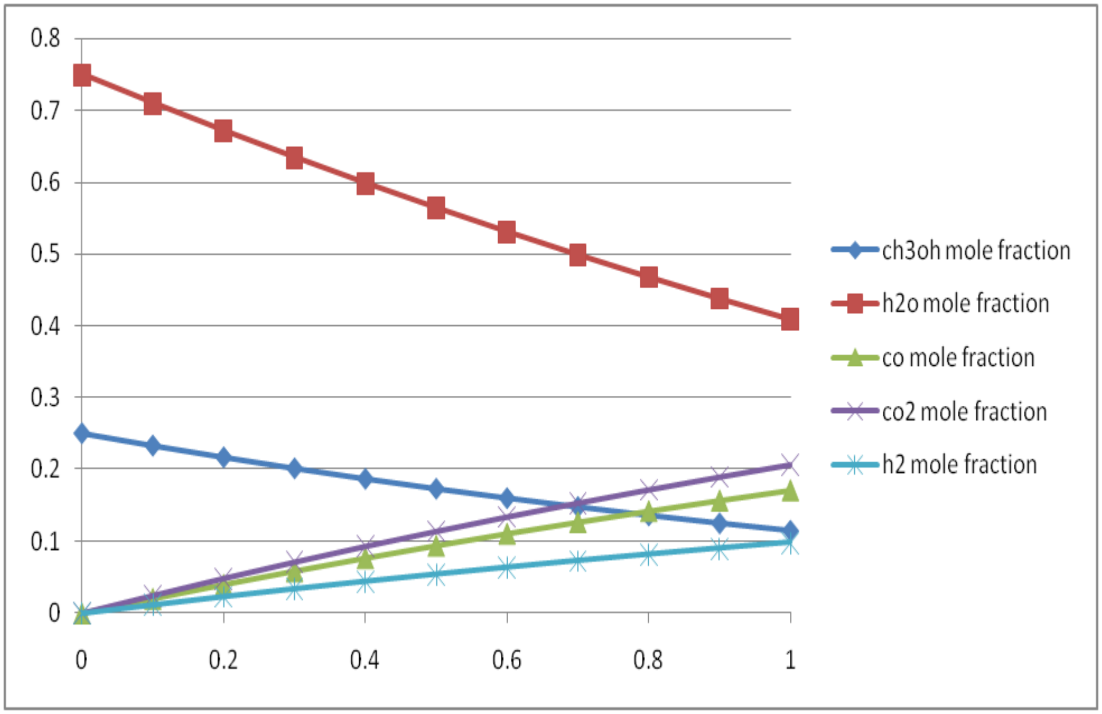
4.1.3 Methanol steam reforming with S/M = 3

i. At T = 437 K

a. Flow rate

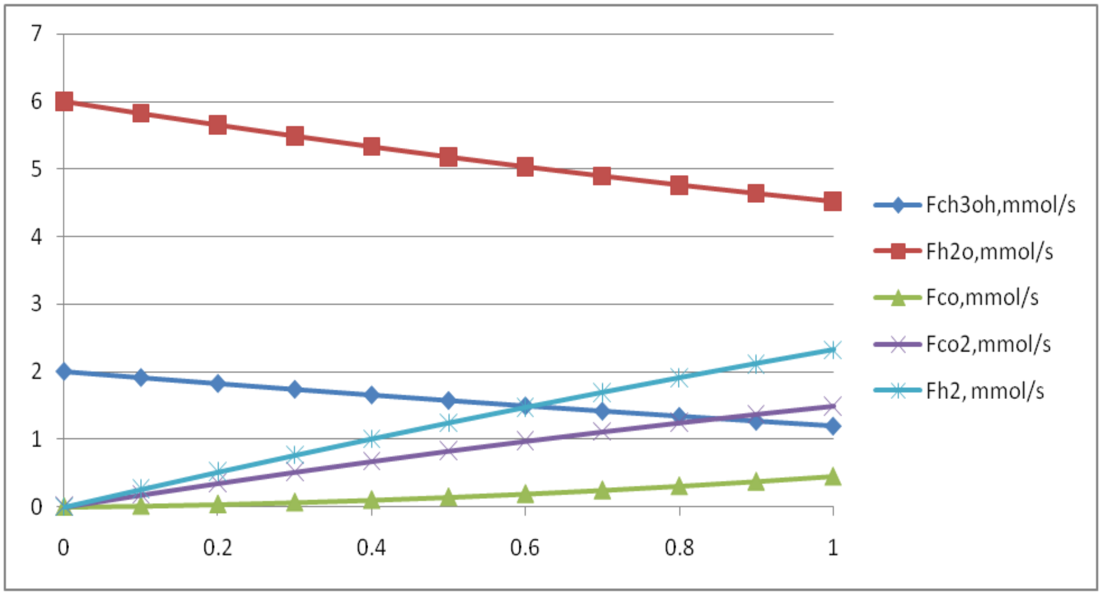


b. Mole fraction

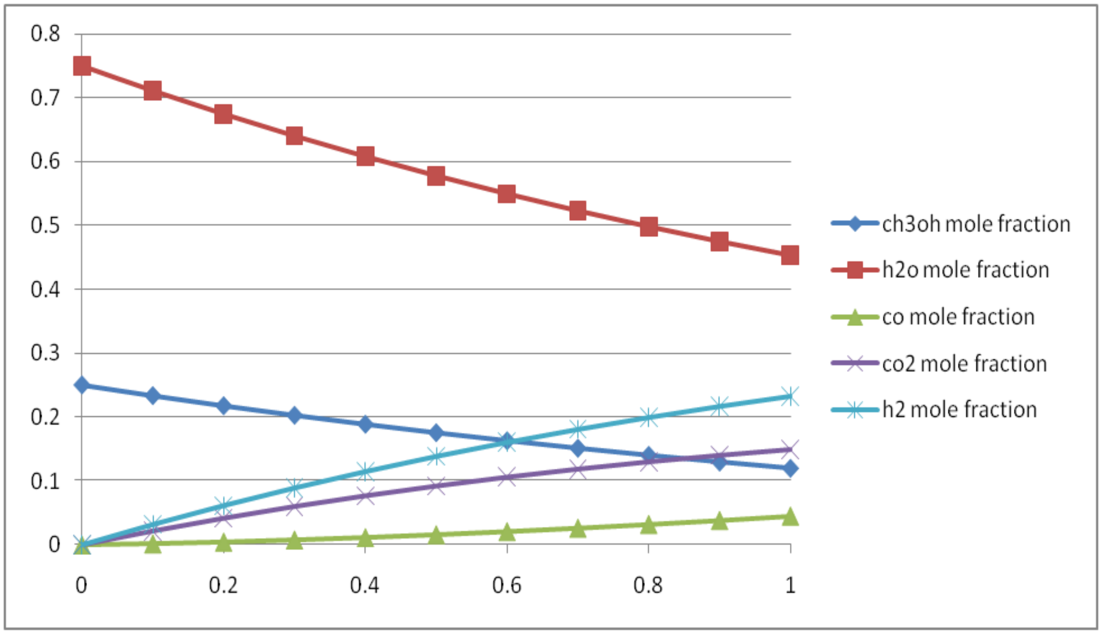


ii. At T = 573 K

a. Flow rate

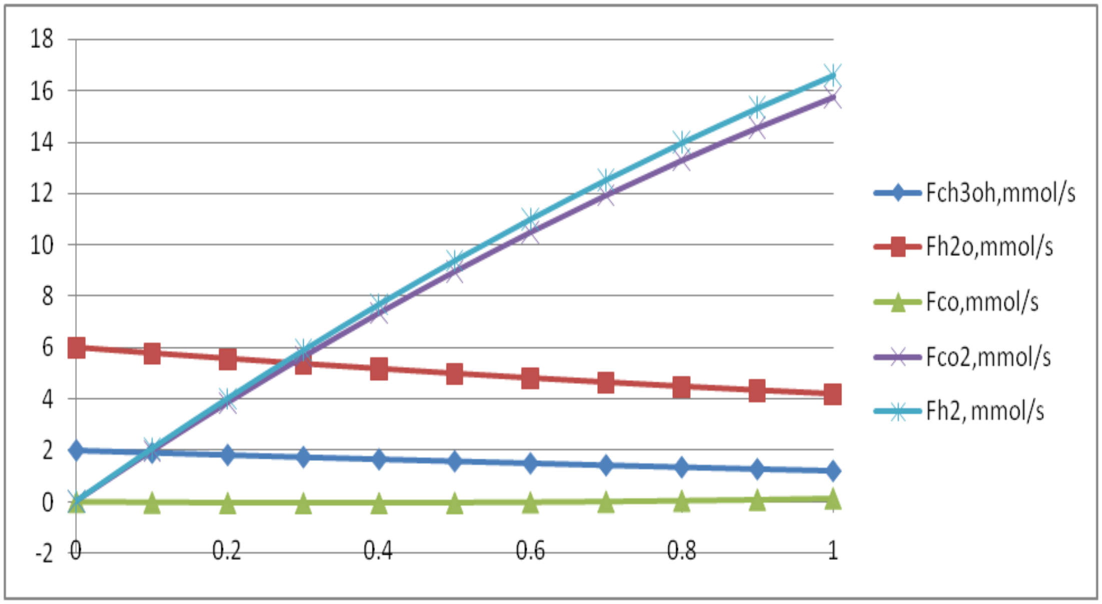


b. Mole fraction

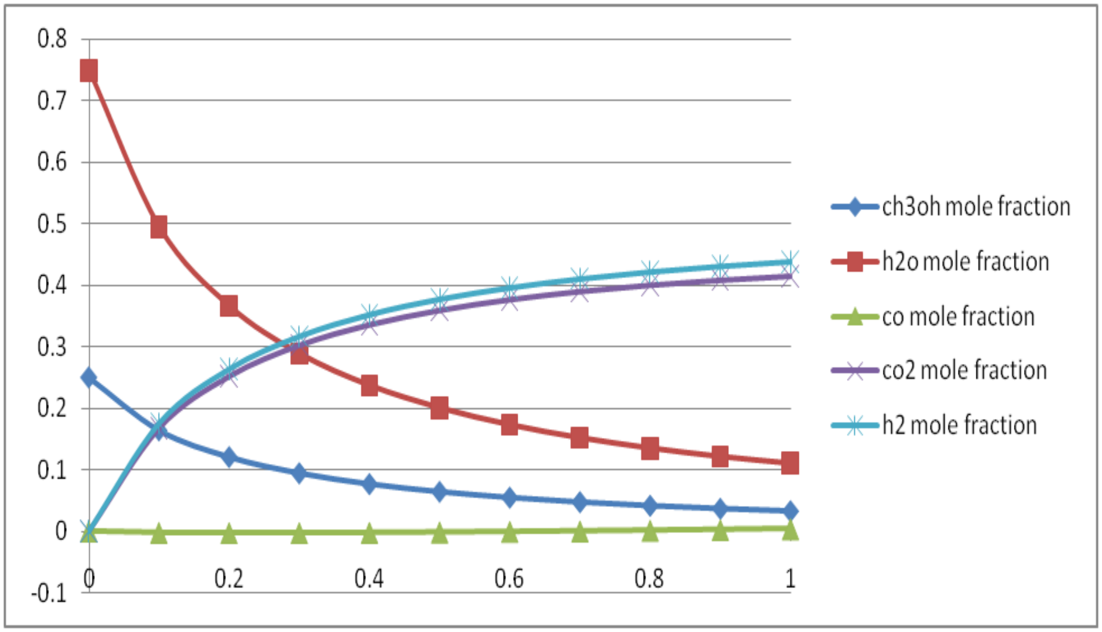


iii. At T = 673 K

a. Flow rate



b. Mole fraction



For the Case 1, the lowest recorded hydrogen, H_2 and Carbon dioxide, CO_2 is at temperature of 473 K and Steam/Methanol (S/M) ratio of 1. While, the highest recorded hydrogen, H_2 produced is at very high temperature and high S/M ratio. The highest recorded flow rate of hydrogen, H_2 produces approximately at 16.5 mmol/s.

Furthermore, simulation results for case 1also shows that the amount of CO_2 produced is almost identical to hydrogen,H_2 produced at very high temperature.

As for the Carbon monoxide, CO, simulation results show that the amount significantly reduced as the temperature increase. However, the S/M ratio show that at S/M = 2, the amount CO produced is very high compared to S/M = 1 and 3. In addition, the simulation results for case 1 shows that the optimum condition in order to produce more hydrogen, H_2 with high purity and lowest achievable CO concentration is at temperature, T = 673 K and S/M = 3.

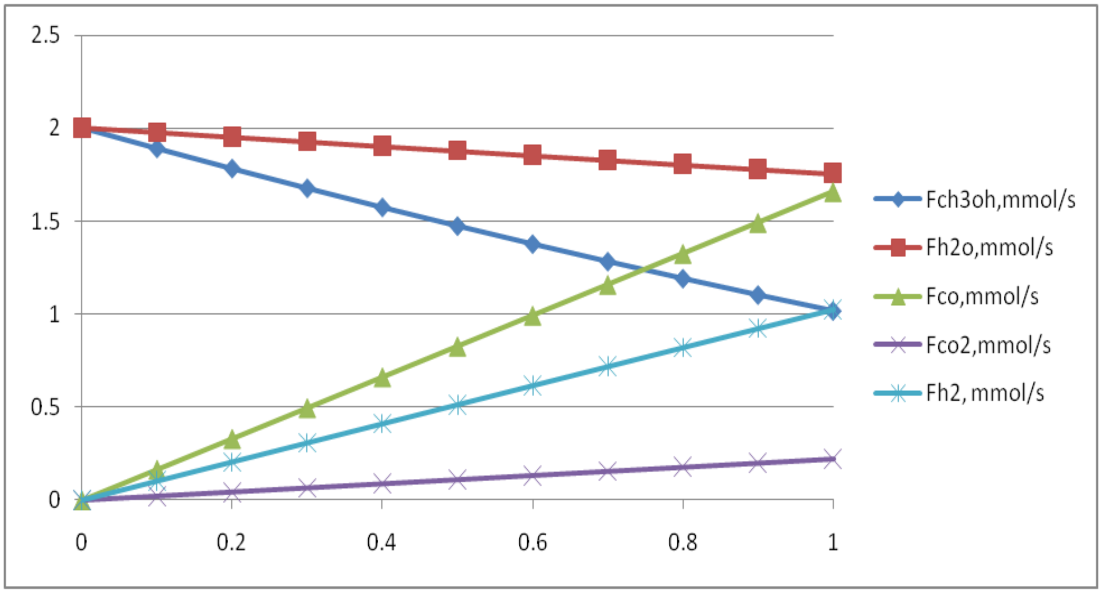
Overall, in case 1, the increase in temperature contributed to the high CO_2 and H_2 production at the outlet of reactor. Based on the graph above, high CO concentration is produced at low temperature whereas the different value of S/M ratio does not affect the CO concentration. The amount of CO produce at low temperature will cause damage at the metal electrocatalyst of the fuel cell anode. Therefore, in order to protect the fuel cell anode lifetime, the amount of CO should be low at 1% of concentration. This simulation result for case 1 show that at T = 673 K and S/M = 3, the lowest CO concentration can be achieved and simultaneously produces more hydrogen, H_2.

4.2 CASE 2 : METHANOL STEAM REFORMING WITH CO_2 REMOVAL

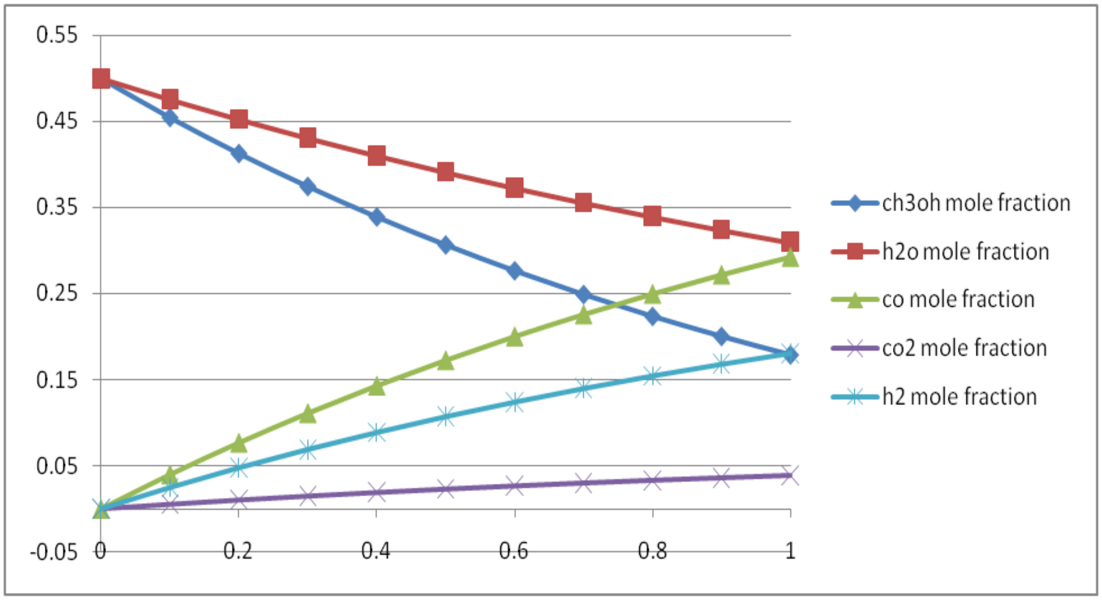
4.2.1 Methanol steam reforming with S/M = 1

i. At T = 473 K

a. Flow rate

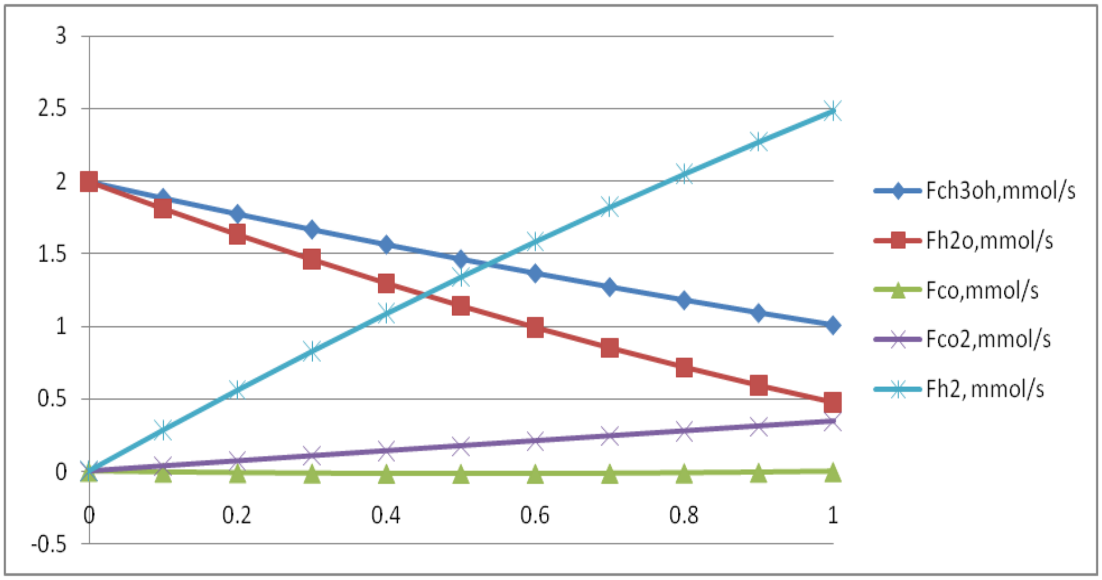


b. Mole fraction

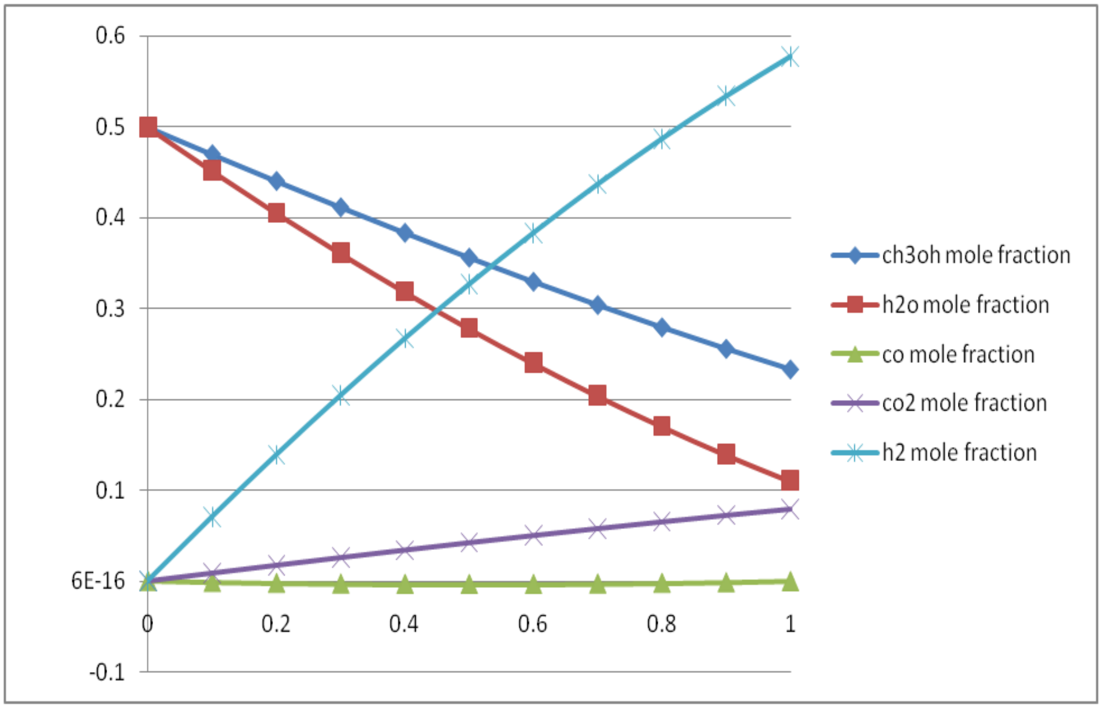


ii. At T = 573 K

a. Flow rate

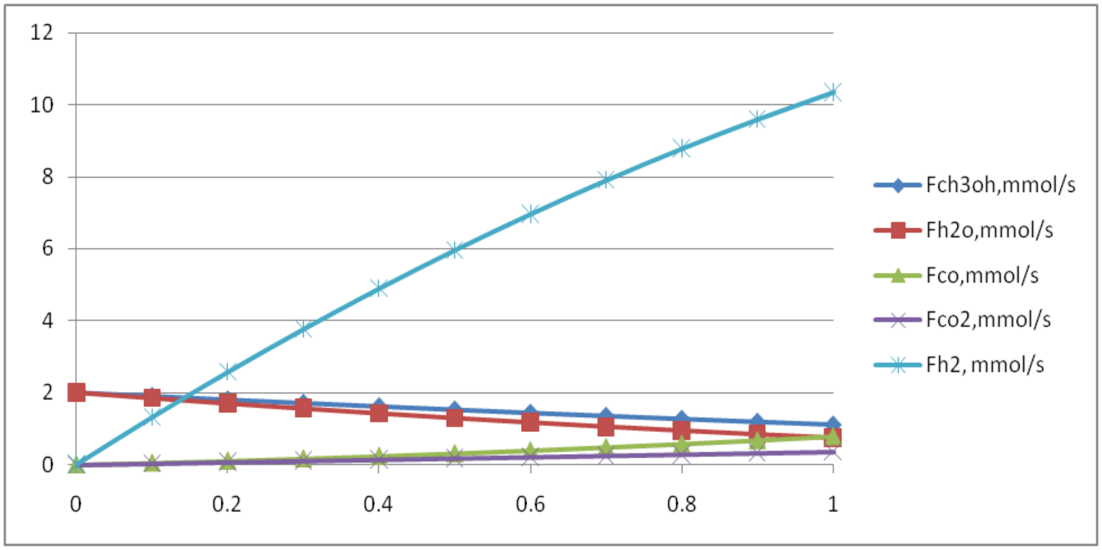


b. Mole fraction

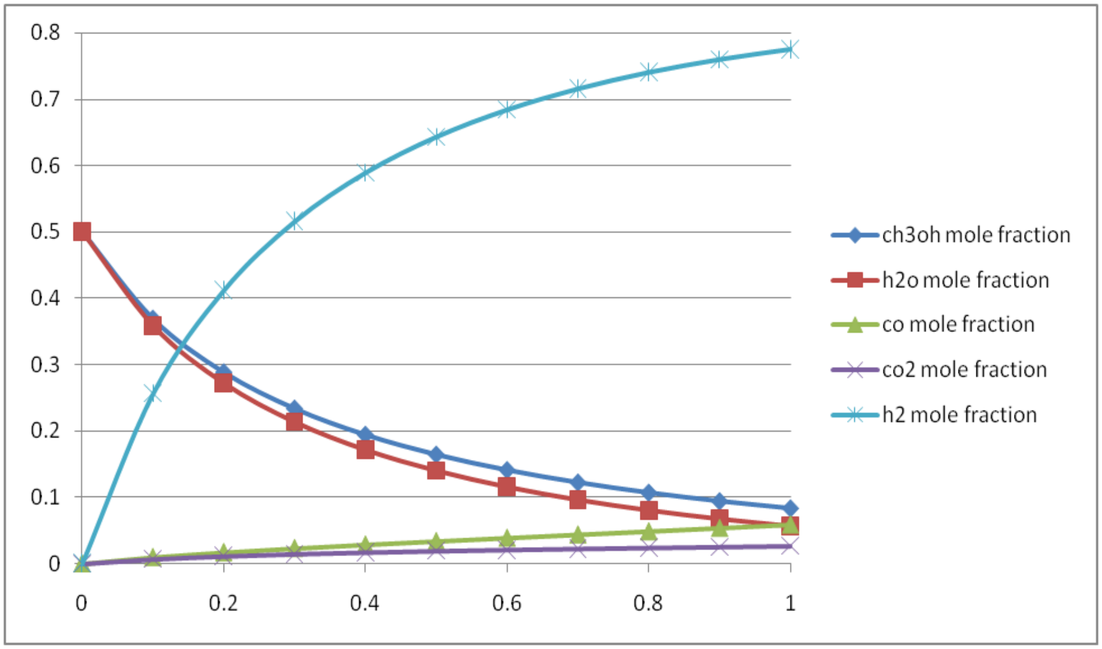


iii. At T = 673 K

a. Flow rate



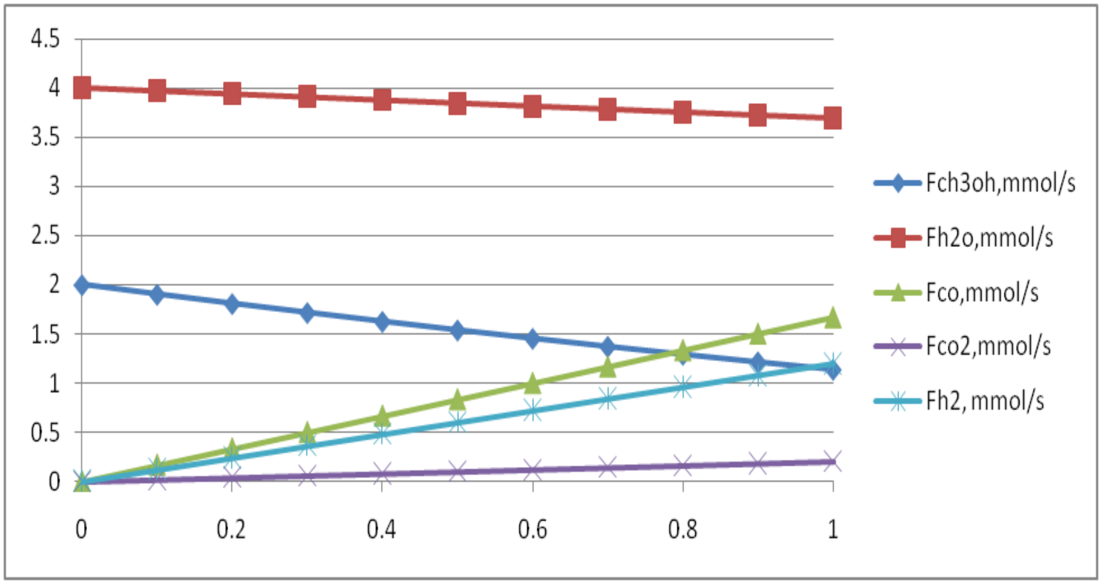
b. Mole fraction



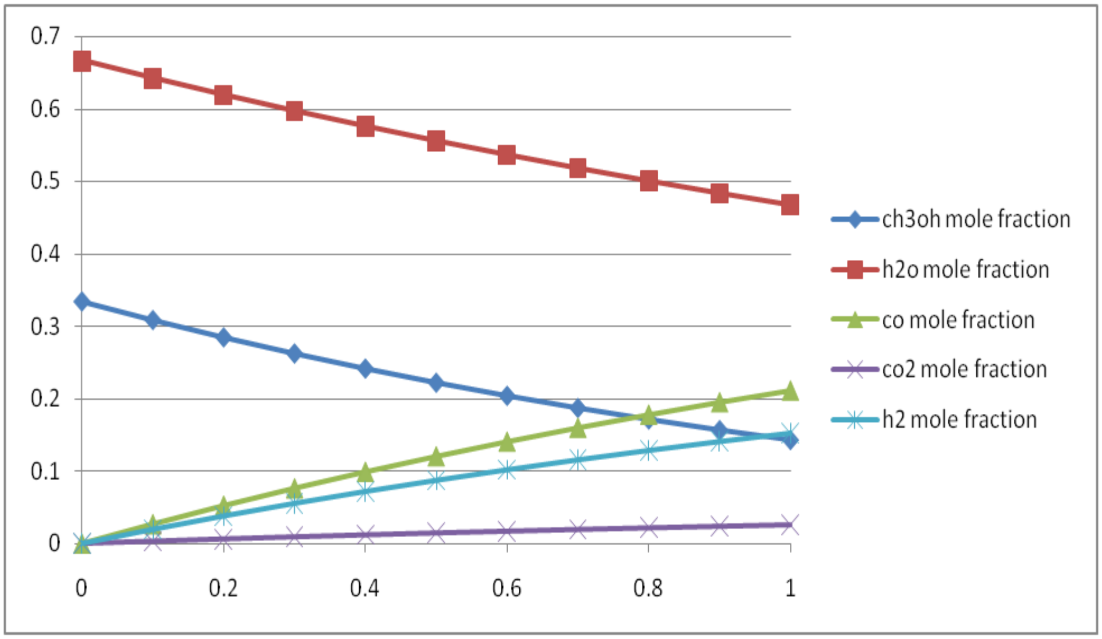
4.2.2 Methanol steam reforming with S/M = 2

i. At T = 473 K

a. Flow rate

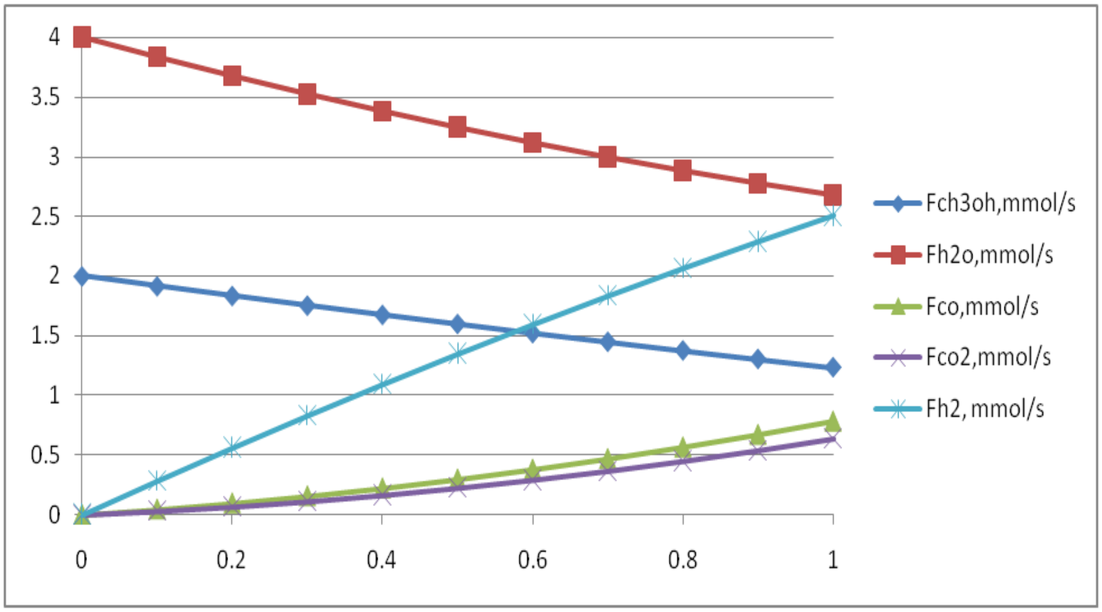


b. Mole fraction

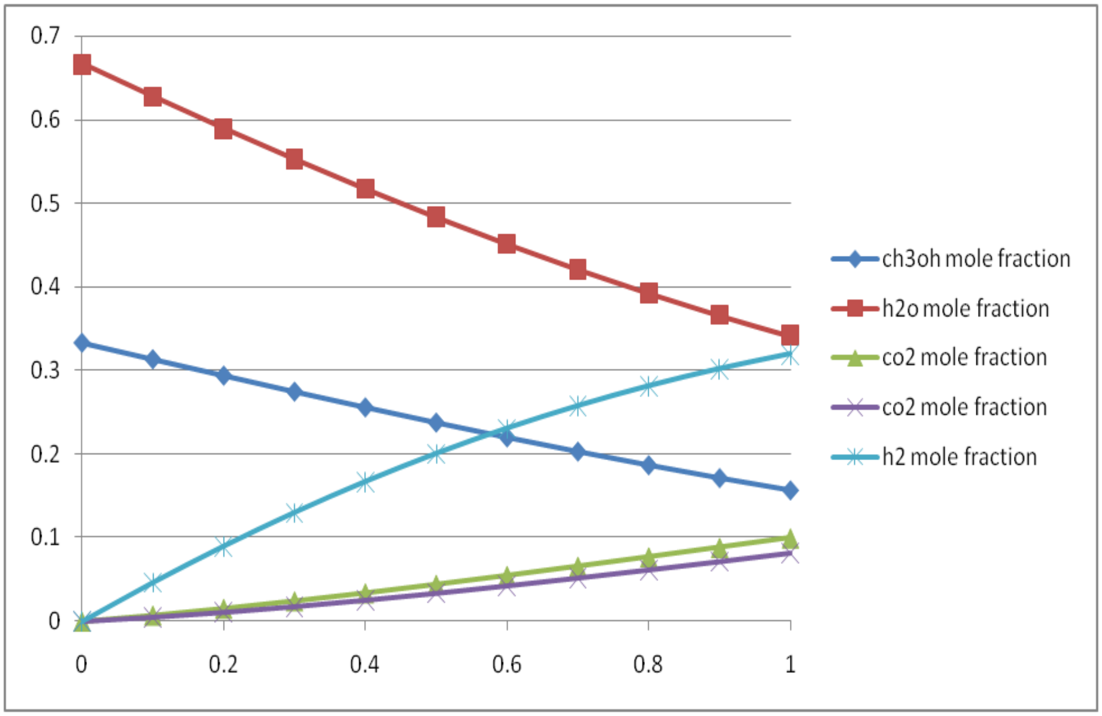


ii. At T = 573 K

a. Flow rate

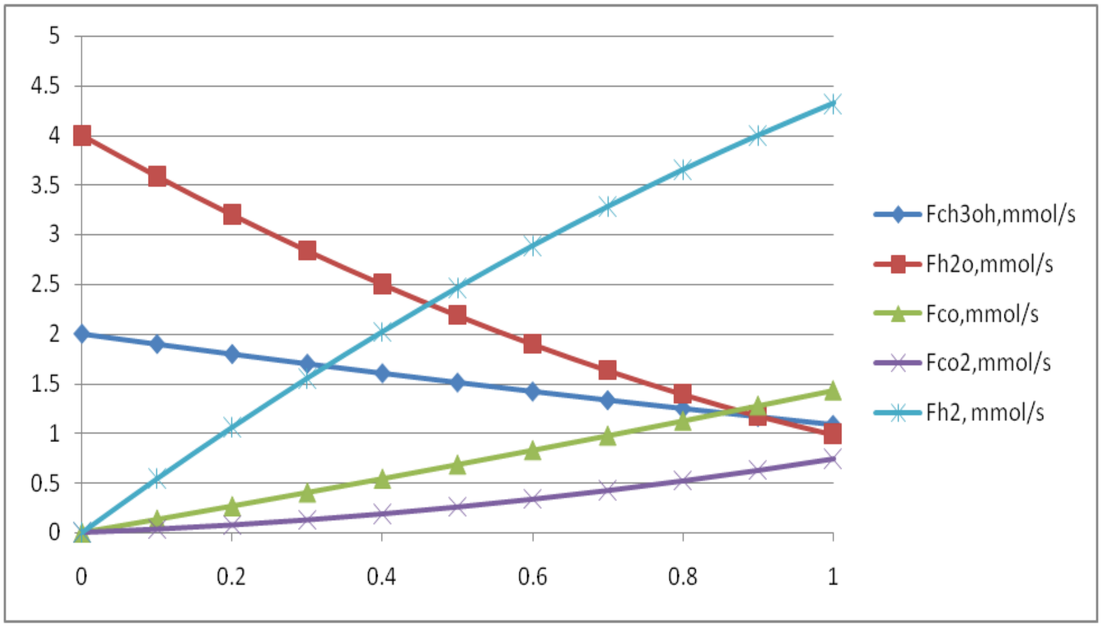


b. Mole fraction

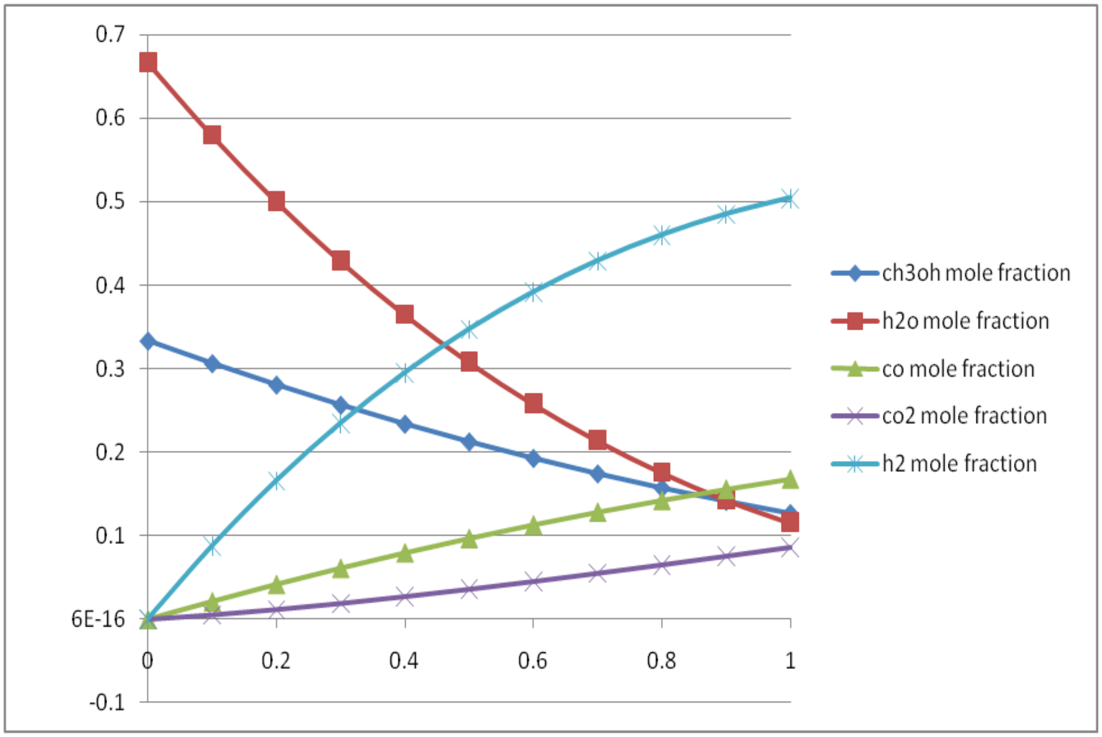


iii. At T = 673 K

a. Flow rate



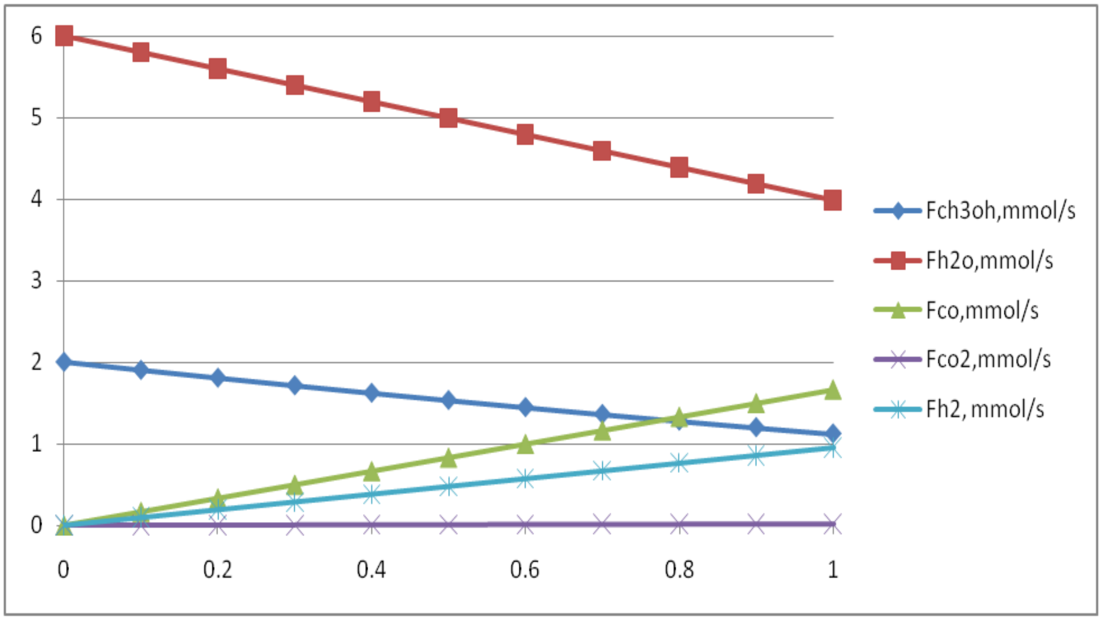
b. Mole fraction



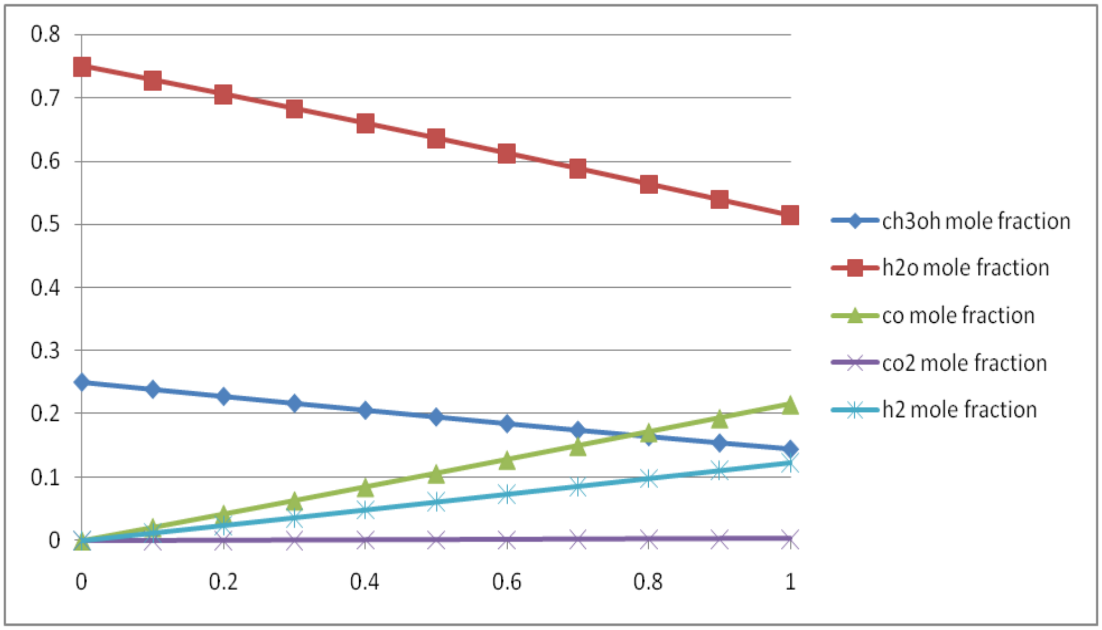
4.2.3 Methanol steam reforming with S/M = 3

i. At T = 473 K

a. Flow rate

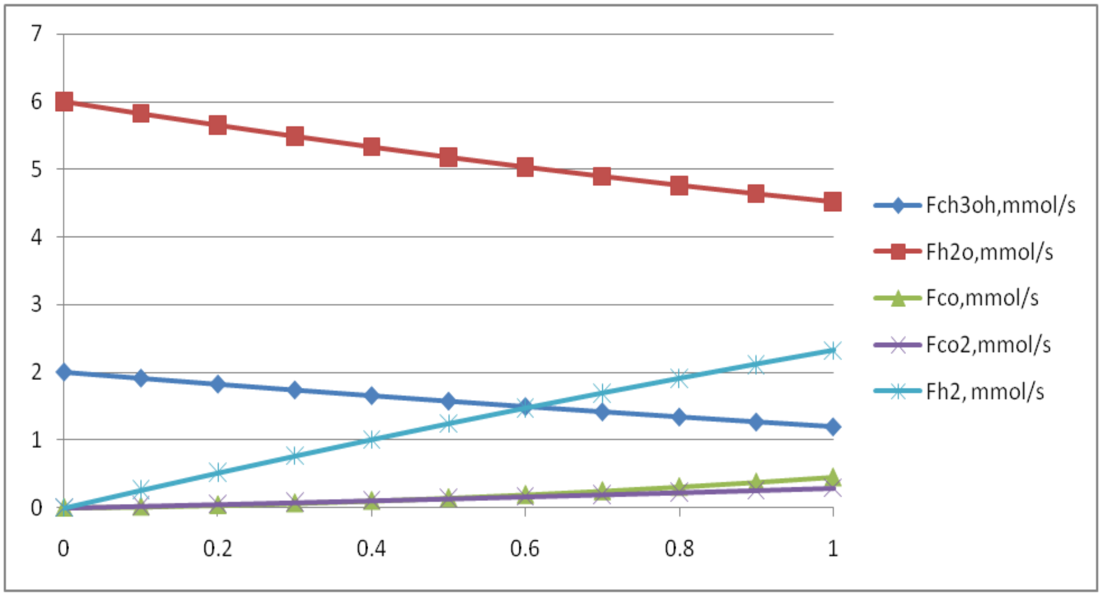


b. Mole fraction

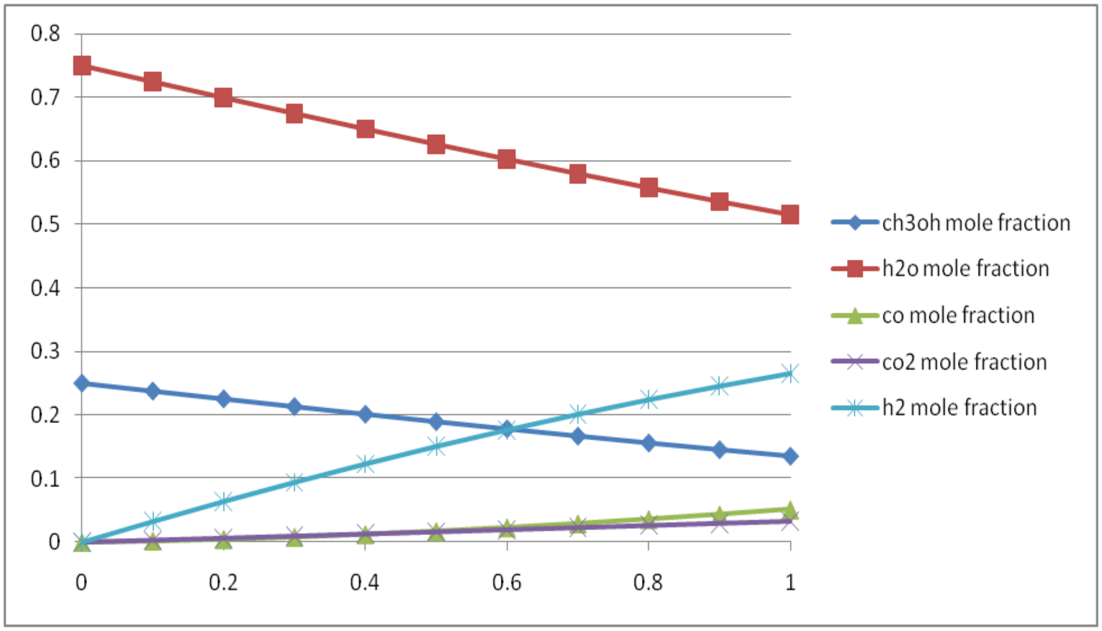


ii. At T = 573 K

a. Flow rate

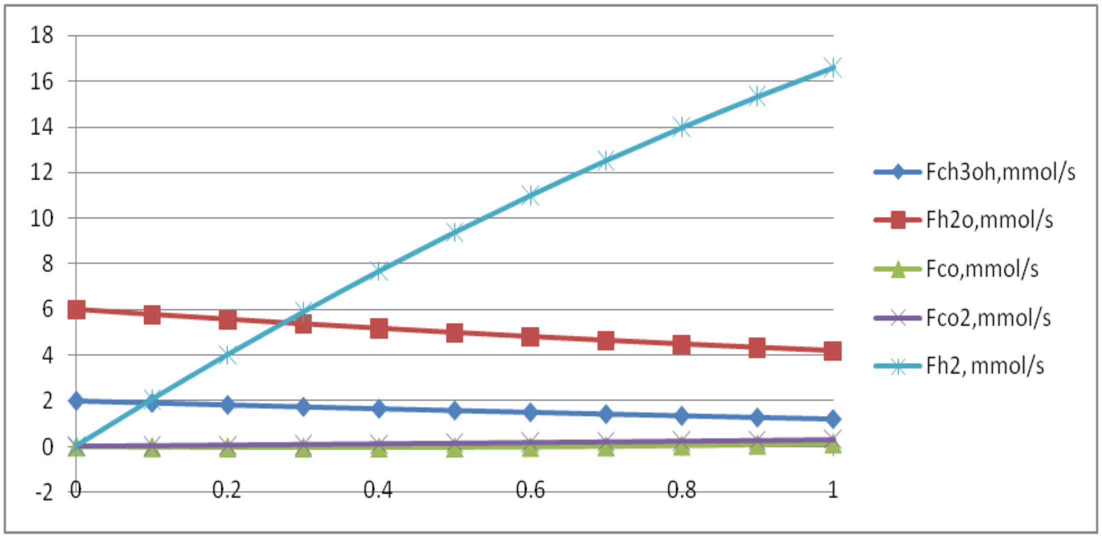


b. Mole fraction

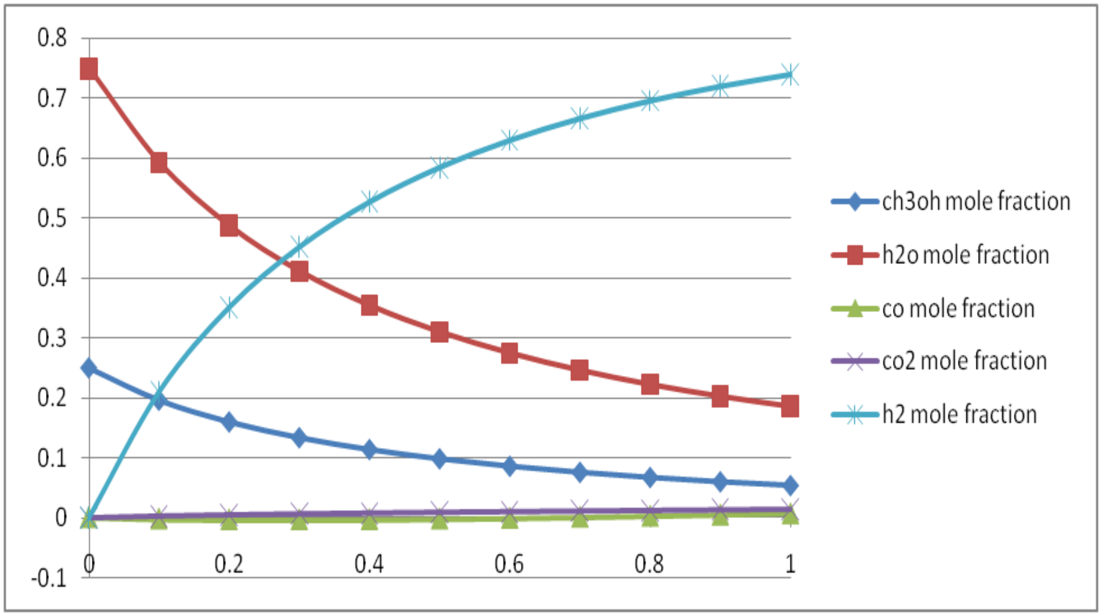


iii. At T = 673 K

a. Flow rate



b. Mole fraction



In case 2, the simulation of methanol steam reforming included with CO_2 adsorption reaction. The function of this reaction is to reduce the amount of CO_2 throughout the reactor. This method is essential in order to produce more concentrated hydrogen, H_2 and CO-free as possible. This method can be further applied by applying a multi-functional catalyst sorbents and adsorbents for CO_2 removal. This idea is base on the Le Chatelier's principle whereas by removing CO_2, the water gas shift reaction (WGS) will move towards CO consumption thus will reduce the CO concentration.

Based on the simulation results, the highest H_2 produced is at T = 673 K and S/M = 3. The H_2 purity also increase which is recorded at 75% while CO concentration almost zero. The amount of other compounds such as CH_3OH and H_2O does not change from without CO_2 removal case but the H_2 purity increase slightly higher from the previous case.

Overall, in case 2, an increase in temperature and S/M ratio will reduce the CO purity. The CO_2 removal only affects at high temperature and high S/M ratio. However at low temperature and S/M ratio, CO_2 removal does not change anything. The optimum condition to produce more hydrogen, H_2 and with CO-free concentration is at T = 673 K and S/M = 3. This condition also applied to the case 1 but the presence of CO_2 adsorbent to adsorb CO_2 increase the H_2 purity by 30%.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

In running the simulation, the reaction mechanism of methanol steam reforming used which is the Peppley model, adequately able to displays the reversibility between the WGS and RWGS reactions depending on the reaction conditions. This is very important in order to study the effect of various conditions for sorption-enhanced steam methanol reforming.

The first case where the results show that at very high temperature, a significant higher methanol conversion and low CO concentration are achieved. But, the various S/M feed ratio does not affect the hydrogen, H_2 and Carbon monoxide, CO produced.

However, based on the case 2 where the CO_2 adsorption reaction mechanism is presence the results analysis is almost identical with case 1. Results shows that at high temperature more hydrogen, H_2 being produced and less amount of CO produced. But the S/M ratio does affects the results as more H_2 concentration and CO free concentration achieved at high S/M ratio. In addition, with the removal of CO_2, high H_2 purity achieved at the outlet of reactor.

Therefore, high temperature and high S/M ratio significantly improve the H_2 production and reduced the amount CO during the sorption-enhanced steam reforming of methanol. With the presence of CO_2 removal reaction, has resulted in increase of H_2 purity and significantly reduced the amount of CO concentration. The Le Chatelier's principle plays its part as reduction in CO concentration is enhanced by removal of CO_2. Lastly, it is very important to achieve a very high H_2/CO ratio to achieve high efficiency and long life of fuel cell anode.

5.2 RECOMMENDATIONS

In order to prove the results of simulation study, a lab-scale experiment on sorption-enhanced steam methanol reforming is recommended. As regards to this simulation study, it is recommended to use other mathematical software than MATLAB in order to improve the data especially in solving the ODE problems. While this simulation project is subject to study on the effects of temperature and S/M ratio which is consists only two variables. Therefore, to find an optimum condition, others variables such as pressure, reactor size can be study.

Furthermore, in running the simulation, the most important factor that contributed to more precise reaction mechanism is the steam reforming reaction kinetic model. Therefore, this can be further enhance by using the updated and improve steam reforming kinetic model. This H_2 production through steam reforming study also can be further improved by using other hydrocarbon candidates such as ethanol, propane and others. A full study on comparison of different hydrocarbon use should look promising where it provide better understanding of steam reforming for H_2 production.

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