CERTIFICATION OF APPROVAL

A Comparative Study of Reforming Technologies: Steam Methane Reforming (SMR), Partial Oxidation (POX) and Auto Thermal Reforming (ATR)

by

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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.

(KARTHIGEYAN A/L MAHINTHERAN)

ABSTRACT

Hydrogen has emerged as an alternative clean source of energy to replace fossil fuels. Hydrogen, a component of syngas, the other being carbon monoxide is usually produced via reforming. Analysis is done to compare three reforming technologies namely steam-methane reforming (SMR), partial oxidation (POX) and auto thermal reforming (ATR). The scope of the study focuses more towards the natural gas reforming, where its main constituent is methane. The operating conditions are manipulated to produce optimum performance and to have the lowest energy cost. Energy cost has become an important factor of consideration in industries. Similar study on comparison of reforming technologies was done using AspenPlus^{TM}. To compare and verify the results of study, the three reforming processes are compared and simulated using HYSYS. Through the simulation, optimum operating conditions for each reforming process is identified. Among the operating conditions varied in process simulation are reactor temperature and steam to carbon ratio for SMR, air ratio and preheat temperature for POX and air ratio, steam to carbon ratio and preheat temperature for ATR. The process is simulated at optimum operating conditions and material and energy balance is done to identify the system with lowest cost in terms of CH_4 equivalent. POX reforming has been identified to have the least cost, requiring 0.3646 mol/s of methane. SMR requires 0.4006 mol/s while ATR requires 0.3668 mol/s of CH_4. Process simulation is also done using plant data and is compared with initial process simulation. Previous study results of Seo.Y.S et al. (2002) were verified and it is comparable to the results in this project.

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ABBREVIATIONS

SMR	- Steam Methane Reforming
POX	- Partial Oxidation
ATR	- Auto Thermal Reforming
S:C	- Steam to Carbon ratio
AR	- Air ratio

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Today, hydrogen has emerged as an alternative clean source of energy to replace fossil fuels. Generally, production of hydrogen from methane is done using one of the three processes: steam-methane reforming (SMR); partial oxidation (POX); auto thermal reforming (ATR). In steam-methane reforming, methane is reacted with steam to produce synthesis gas. Partial oxidation (POX) is a process of reforming methane with air while auto thermal reforming is a combination of POX and SMR reforming. Compared to steam-methane reforming process, partial oxidation and auto thermal reforming are relatively new technologies. Meanwhile, steam-methane is the most widely used reforming method currently. Reaction of steam and methane is endothermic while reaction between oxygen and methane is an exothermic reaction.

Basically, reforming is a process of changing the form or converting fuel like natural gas, heavy hydrocarbons and naphtha to produce synthesis gas. This study is more focused on the reforming of natural gas to produce synthesis gas namely hydrogen, H_2 and carbon monoxide, CO. Reforming process usually consists of desulphurization process, reforming reactor, shift reactor and purification process.

Before any research is done, problem statement and objectives of research are determined. Justification of the study is given. Based on that, scope of study is determined. Methodology and tools to be used during study are also identified.

1.2 PROBLEM STATEMENT

Energy has become an important topic of concern in recent days. Various efforts of energy conservation are being taken in industries. In the case of natural gas reforming which mainly comprises of methane, there are three types of technologies namely steam-methane reforming (SMR), partial oxidation (POX) and auto thermal reforming (ATR). As energy is becoming a critical source day by day, there is a need to analyze and identify the best reforming method operating in optimum conditions and has the lowest energy cost. A study on the evaluation of thermodynamically favourable operating conditions for three different reforming technologies was done by Seo Y.-S, et al. (2002). AspenPlus^{TM} was used to determine the reforming method having the lowest energy cost. Therefore, there is a need to compare and verify the results obtained using different software for process simulation. The simulation results are also to be compared with data obtained from industry to produce a more complete analysis.

1.3 OBJECTIVES AND SCOPE OF STUDY

Study is done to compare the three reforming methods, which are steam methane reforming (SMR), partial oxidation (POX) and auto thermal reforming (ATR). Natural gas is widely used to produce hydrogen gas for industry. The reforming studies done are more focused to methane as the feed, which is the main constituent of natural gas. The objectives of this study are:

1. To do a comparative analysis of three different reforming technologies namely steam-methane reforming(SMR), partial oxidation(POX) and auto thermal reforming(ATR) for production of synthesis gas.

2. To evaluate and manipulate operating conditions of reforming for optimum performance using process simulation.

3. To identify the favourable reforming method having the highest efficiency in terms of lowest energy consumption.

4. To verify the findings of prior study that used AspenPlus^{TM} for process simulation.

5. To compare process simulation done with plant data from industry.

CHAPTER 2

LITERATURE REVIEW

This chapter is on the literature review done during the research project. Study was done on the basics of reforming process. Reforming process can be divided into few stages mainly pretreatment, reforming reaction, water gas shift reaction and purification process. Four types of reforming process were reviewed. They are steam methane reforming (SMR), partial oxidation (POX), auto thermal reforming (ATR) and dry reforming (CO_2 reforming). SMR involves oxidation of hydrocarbon by steam while POX uses air. ATR is basically a combination of SMR and POX, where both the endothermic reaction with steam and exothermic reaction with oxygen occurs, converting the hydrocarbon to synthesis gas. Dry reforming was studied but not taken into the comparison study as it has a low H_2/CO, which produces less hydrogen. As the objective is to identify the reforming method having the least cost to produce 1 mol/s of hydrogen, dry reforming is not included in the study.

2.1 PRODUCTION OF SYNTHESIS GAS

Production of synthesis gas via reforming has been increasing in recent years to meet the increasing demand for hydrogen. Hydrogen is an important raw material in the petrochemical and chemical industries. Large quantities of hydrogen are used to produce ammonia and methanol. Hydrogen has also emerged as an alternative clean energy source to the existing fossil fuels. It can be directly combusted in an internal combustion engine or electrochemically converted to electricity in a fuel cell system. Hydrogen is identified as a clean source of energy as it is combusted to produce energy and pure water unlike fossil fuels which will release carbon components.

Hydrogen is mainly produced from reforming of natural gas and other light and heavy hydrocarbons. Heavier hydrocarbons are normally converted by partial oxidation method. The most general reforming method, which is steam methane reforming is normally used for lighter hydrocarbons like C_1, C_2 and C_3. Steam methane reforming (SMR) is the oldest and most widely used reforming method. However, it has a disadvantage of slow start up. Lately, partial oxidation (POX) and auto thermal reforming (ATR) have attracted much interest.

2.2 INTRODUCTION TO REFORMING PROCESS

Reforming process is basically where the raw material for example natural gas is converted into synthesis gas, namely hydrogen (H_2) and carbon monoxide (CO). A complete reforming system comprises of pretreatment process, reforming reactor, shift conversion reactor and gas purification process. Pretreatment normally comprises of hydro treating and desulphurization. Hydro treating is a process where a controlled volume of pure hydrogen is mixed with feed gas to saturate any olefins present before the gas enters the reformer. Olefin concentrations of in excess of 3 to 5 parts per million (ppm) will cause coking to occur on the reformer catalyst. Coking will subsequently cause increased pressure drop, uneven flow through reformer tubes, hot spots on the tubes and eventual destruction of the catalyst. For example, olefins such as propylene and butylene react with hydrogen to form propane and butane respectively.

$$C_3H_6 + H_2 \longrightarrow C_3H_8$$
$$C_4H_8 + H_2 \longrightarrow C_4H_{10}$$

In addition to that, all other sulphur compounds in the feed will also react with hydrogen forming hydrogen sulfide. An example is as follows:

$$2H_2 + S_2 \longrightarrow 2H_2S$$

The feed gas is then passed through the catalyst beds of desulphurizer vessel. An example of catalyst used is zinc oxide. Zinc oxide functions to adsorb the sulfur compounds. The gas exiting the desulphurizer will have almost zero content of sulphur. Sulphur compound must be removed from the feed gas as it severely deactivates the reformer and shift reactor catalyst, especially in the case of low reforming temperatures.

After pretreatment, the desulphurized feed gas will undergo reforming reaction. Natural gas will be reformed to produce synthesis gases, namely hydrogen and carbon monoxide, carbon dioxide, unconverted methane, water (H_2O) and other radicals. Catalysts used for reforming usually consist of transition metal, particularly nickel (Ni) and rhodium (Rh). Transition metal is considered to be most promising since noble metals have high cost and limited availability. The choice of suitable operating conditions relating to catalyst stability and process safety is requires much attention. At industrial conditions, high temperatures and pressures could cause hot spot formation that could cause severe catalyst deactivation. Types of reactors differ for different types of reforming. For example steam methane reforming normally comprises of a multi tubular reactor. Inside the reactor, there are catalysts packed tubes where the reactants flow through and undergo reforming. As this particular reforming reaction is endothermic, heat need to be supplied to sustain the reaction temperature. Therefore, steam methane reformer normally comes together with a furnace where combustion occurs to supply the heat needed by reforming reactor.

The main products of reforming reaction are hydrogen and carbon monoxide. Release of carbon monoxide is practicable as it is a very poisonous gas. Therefore, carbon monoxide is converted to carbon dioxide by shift conversion. Carbon monoxide is reacted with steam to produce carbon monoxide and hydrogen.

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Water gas shift reaction not only decreases carbon monoxide released but also increases the yield of hydrogen in a reforming process. Water gas shift reactors can be classified as one of two types according to their working temperature. A high-temperature shift reactor is operated around 400°C while a low-temperature shift converter is operated around 200°C. The carbon monoxide concentration exiting the shift reactor is lower than 1.0%.

The final stage of reforming process is gas purification. Unit operation usually used for gas purification is the adsorption column. Purity of hydrogen gas produced will be determined by this process. Carbon dioxide, carbon monoxide and moisture are adsorbed by adsorbent. Examples of adsorbents used in the adsorption column are activated carbon and activated alumina. The hydrogen gas will be compressed before stored in the storage tank. Impurities adsorbed will be purged out of the system through a vent. If the overall conversion of natural gas is lower, the unconverted reactant will be collected after the adsorption column and before the venting.

2.3 STEAM METHANE REFORMING (SMR)

Steam methane reforming is the oldest and most widely used method to produce synthesis gas. In this reforming method, natural gas where its main constituent is methane is reacted with steam to form mainly hydrogen (H_2) and carbon monoxide (CO). The basic equation for the reforming reaction can be written as

$$CH_4 + \beta H_2O \longrightarrow \text{products}$$

where, β is stoichiometric coefficient

The products can be unconverted methane (CH_4), hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), solid carbon (C), moisture (H_2O) and other radicals such as H, O, OH, HO_2, HCO, CH and CH_2. This reforming reaction is endothermic, therefore it needs continuous heat supply to maintain the reactor operating temperature.

An important parameter in steam methane reforming is the steam to carbon ratio, S:C. It can be defined as

Steam to carbon ratio (S:C) = (molar flow rate of steam / carbon molar flow rate in CH_4)

Theoretically, when steam to carbon ratio is increased, methane conversion will increase. When amount of reactant, steam is increased, equilibrium is shifted. To achieve equilibrium, the reaction will move forward to produce more products hence reducing the amount of unconverted reactant. However, increasing steam to carbon ratio only is not enough to achieve conversion of 99%. Reactor temperature must also be increased to achieve the desired methane conversion.

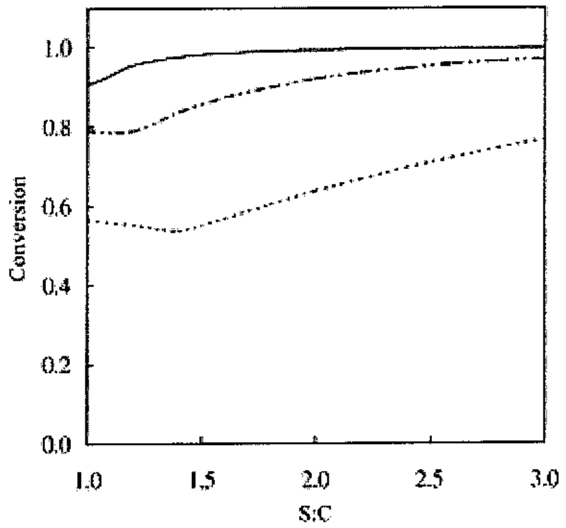


Figure 2.1: Effect of increasing S:C on methane conversion

(Source: Seo.Y.-S et al. 2002)

Apart from S:C, other parameters which affects the conversion and equilibrium composition of SMR reactor are reactor temperature and pressure. Y.-S.Seo (2002) stated that when the reactor temperature is raised from 600 to 800°C, the conversion increases from 0.56 to 0.90. If the operating temperature of the reactor is limited to less than 800°C in order to maintain thermal durability of the catalyst, then it can be seen that it is difficult to obtain a satisfactory conversion that is greater than 0.99 (pg. 215). Reactor temperature also significantly affects the formation of solid carbon. Y.-S.Seo (2002) stated that solid carbon is likely to be generated at temperature of less than 850°C with a S:C of 1.0 and at 1.0 bar reactor pressure. This implies that in order to avoid coke formation, the reactor temperature should be maintained at temperatures that are greater than 850°C. On the other hand, keeping the reactor temperature above 850°C is likely to damage the thermal durability of the catalyst (pg. 215). Based on the study conducted by Y.-S.Seo, reactor temperature of 800°C is found to be optimum as there is no formation of solid carbon.

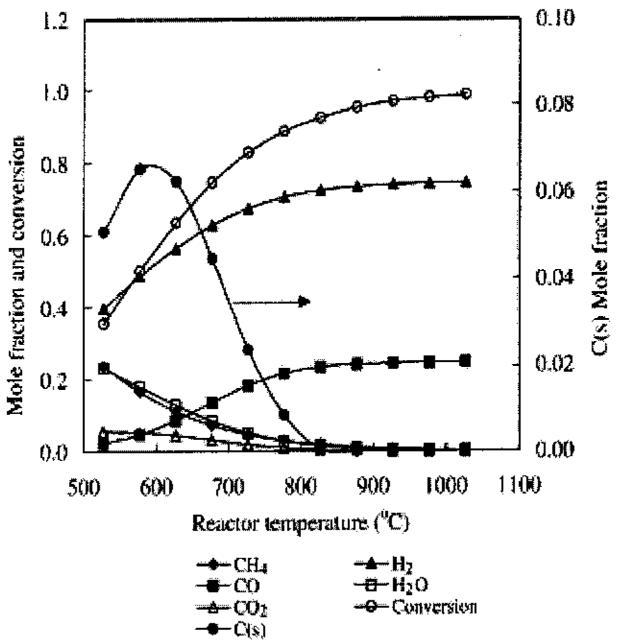


Figure 2.2: Effect of increasing reactor temperature on equilibrium compositions of reactor. (Source: Seo.Y.-S et al. 2002)

Before entering the reforming reactor, the feed is first preheated. Equilibrium compositions of SMR reactor are independent of the preheat temperature of feed. This is because the reactor temperature is already fixed at a certain value. Operating temperature of SMR reactor is determined by the external heat transfer to the reactor. Therefore, preheat temperature only affects the heat duty that is transferred to the SMR reactor. One of the frequently used methods to transfer the heat is using a furnace, where the reforming tubes are built in.

Reactor pressure also effects the conversion and equilibrium compositions in the reactor. From literature review, it is found that when reactor pressure is increased, the conversion reduces. Mole fractions of hydrogen and carbon monoxide also rapidly reduce when operating pressure of reactor is increased. Conversely, the mole fraction of H_2O increases with pressure. Therefore it is desirable to keep the pressure of SMR reactor as low as possible.

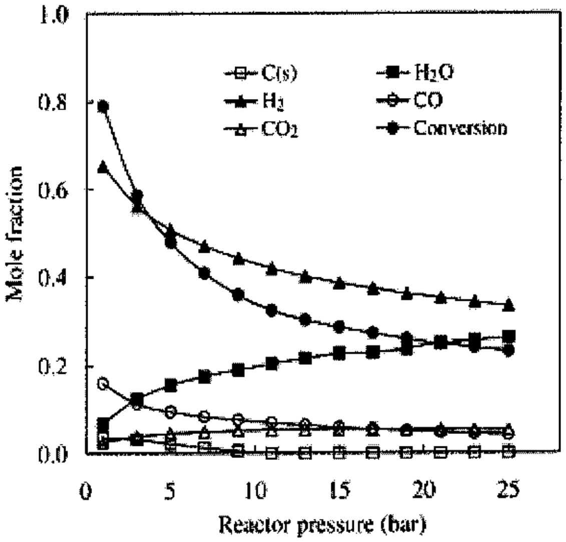


Figure 2.3: Effects of the pressure on the equilibrium compositions and conversion in SMR reactor. Reactor temperature, 700°C; S:C ratio, 1.0. (Source : Seo.Y.-S et al. 2002)

2.4 PARTIAL OXIDATION (POX)

Partial oxidation reforming is relatively a new method compared to steam methane reforming. Partial oxidation is a reforming process where methane is oxidized sub-stoichiometrically to form hydrogen and carbon monoxide. The general reaction mechanism for POX reforming reactor can be written as follows:

$$CH_4 + \alpha O_2 + 3.77\alpha N_2 \longrightarrow \text{Products}$$

where α is stoichiometric coefficient

This reforming reaction is exothermic. Therefore heat has to be removed by a cold stream to stabilize the reaction temperature. Overheating could create hotpots damaging the catalyst and cause runaway reaction. The important parameter in partial oxidation is the air ratio:

$$\text{Air ratio} = 0.5\ (\text{molar flowrate of } O_2 / \text{molar flowrate of } CH_4)$$

By controlling the amount of air fed into the reformer, oxidation level is being controlled. As air ratio is increased, methane conversion increases. When air ratio increased, more oxygen is supplied to the system. Therefore, more methane reacts with oxygen to produce synthesis gas. However, oxygen supply must not be more than the sub-stoichiometric level to promote partial oxidation, which yields hydrogen and carbon monoxide. If oxygen is supplied in excess, full oxidation is favourable and methane will be oxidized to form carbon dioxide and water. High air ratio will also encourage oxidation of hydrogen.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

If air ratio is too low, there is tendency for coking to occur. Y.-S.Yeo (2002) says that coking boundary is situated at an air ratio of 0.3. In the coking region, which corresponds to an air ratio range of 0.0 to 0.3, C(s) increases to a peak near an air ratio of 0.1, reduces and finally drops to zero at an air ratio of 0.3 (pg. 217). This result was achieved by coke formation modeling. Figure below is the equilibrium profile obtained.

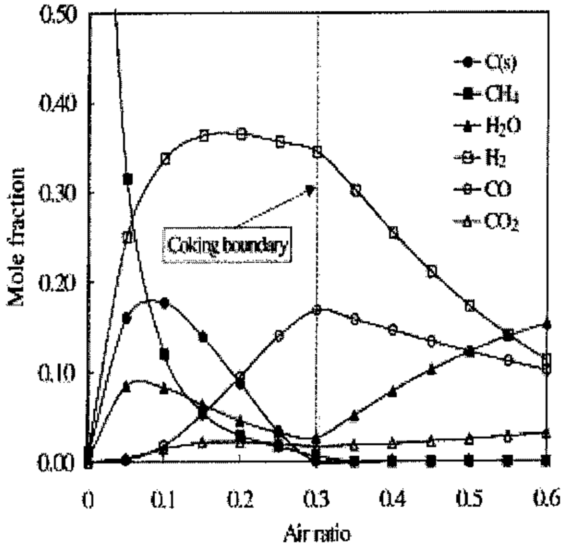


Figure 2.4: Equilibrium composition of POX reactor with regard to air ratio. Preheat temperature of reactants, 200°C; reactor pressure, 1.0 bar. (Source: Seo.Y.-S et al. 2002)

Conversion in the reforming reactor is measured by identifying the amount of methane (reactant) being converted. Hydrogen yield is measured by the ratio of hydrogen produced to methane converted.

Methane Conversion = $(CH_{4\,in} - CH_{4\,out}) / CH_{4\,in} \times 100\%$

H_2 yield = $(H_{2\,out}) / (CH_{4\,in} - CH_{4\,out}) \times 100\%$

Y.-S.Seo (2002) stated that the POX reforming reactor is modeled at adiabatic conditions during the calculation of the equilibrium state, which means that there is no heat transfer to or from the POX reactor (pg.216). Unlike steam methane reforming, preheat temperature of reactants (CH_4 and air) can exert an important effect on the POX reforming reactor. Prior to entering the reactor, reactants should be heated to a certain temperature to sustain the catalytic reaction of the reforming catalysts. However, preheat temperature cannot be very high as it could increase the operating temperature of adiabatic reactor and damage the catalysts.

2.5 AUTO THERMAL REFORMING (ATR)

Auto thermal reforming is a combination of both steam methane reforming and partial oxidation reforming. Auto thermal reforming is a relatively new method of reforming where methane is reacted with both air and steam. The general reaction mechanism for auto thermal reforming reactor can be written as follows:

$$CH_4 + \alpha O_2 + \beta H_2O + 3.77\alpha N_2 \longrightarrow \text{Products}$$

In the reforming reactor both endothermic and exothermic reactions take place. Zhong Wen Liu (2002) stated that oxy-steam reforming, which integrates partial oxidation and steam methane reforming, has many advantages such as: low energy requirements due to the opposite contribution of the exothermic methane oxidation and endothermic steam reforming (pg. 285). As with the partial oxidation system, the auto thermal reforming reactor is maintained under adiabatic conditions, which means that there is no heat transfer to or form the reactor. The adiabatic temperature of reforming reactor is determined by manipulating input conditions of air ratio, S:C, preheat temperature and reactor pressure.

Air ratio and steam to carbon ratio significantly affects the conversion and adiabatic temperature. Conversion will rapidly increase when air ratio is increased till a point where the conversion remains at 100%. This is because the excessive O_2 is used to oxidize H_2 and CO into H_2O and CO_2.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$2CO + O_2 \longrightarrow 2CO_2$$

As steam to carbon ratio is increased, theoretically hydrogen to carbon monoxide ratio, H_2:CO to increase. Steam to carbon ratio is increased by increasing the amount of steam fed to the reactor. When steam is increased, extra H_2O in reactor will react with carbon monoxide to produce carbon dioxide. This is referred to as water gas shift reaction. The shift reaction will produce more hydrogen, hence increasing the yield of hydrogen and hydrogen to carbon monoxide ratio. However, this theory is only true till a certain steam to carbon ratio where the H_2:CO ratio then decreases. This is caused because of the faster rate of oxidation of hydrogen than carbon monoxide. Therefore, the yield of hydrogen will decrease.

Reactants to the auto thermal reforming reactor will be preheated to sustain certain temperature for oxidation of methane. If the preheat temperature is increased while other parameters like steam to carbon ratio and air ratio is kept constant, operating temperature of reforming reactor will increase. This will result in a higher total conversion of methane.

This type of reforming is referred as auto thermal because by using the right mixture of fuel, air and steam, partial oxidation reaction supplies the heat required to drive the catalytic steam methane reforming reaction. Unlike steam methane reformer, auto thermal reformer requires no external heat source. This makes auto thermal reformer more compact and it is more likely for auto thermal reformer to have a lower capital cost than steam methane reformer. Auto thermal also typically offers high heat transfer efficiency as compared to partial oxidation reforming because the excess heat is not easily recovered.

Favourable operating conditions of the auto thermal reforming, the adiabatic reactor temperature and conversion can be determined by manipulating the steam to carbon ratio and air ratio.

2.6 DRY REFORMING (CO_2 REFORMING)

Dry reforming is where carbon dioxide, CO_2 is reacted with CH_4 to produce synthesis gas namely hydrogen and carbon monoxide. Reforming with CO_2, rather than H_2O is attractive because it is employed in areas where water is not available and syngas with a lower H_2/CO ratio. Yield of syngas with a lower H_2/CO is particularly utilized in Fischer Tropsch synthesis of long chain hydrocarbons. The general reaction mechanism for dry reforming is:

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO$$

From the stoichiometric equation, it can be seen that more carbon monoxide is formed through reforming reaction. Therefore, there is more tendency for carbon deposits to be formed through Boudouard reaction, where carbon monoxide breaks up to form carbon monoxide and solid carbon. Existence of solid carbon could promote coking at the reformer tubes, causing hot spots to occur. This will reduce the heat transfer efficiency and deactivate the catalyst. Therefore, the frequency of changing catalysts will be higher for dry reforming. This will increase the total operation cost.

As this study is more focused on the production of hydrogen, this type of reforming is not viable as it has a low H_2/CO ratio. Therefore, this dry reforming was not analyzed in this study.

CHAPTER 3

METHODOLOGY / PROJECT WORK

This chapter explains the methodology of the research project. The project work done in order to obtain the results is also discussed. The project work can be divided into three main parts which are the comparative analysis, process simulation and comparison of process simulation results with plant data.

3.1 METHODOLOGY

The research project starts by defining the problem statement and the objectives of study. The purpose and importance of this study is underlined briefly in the problem statement. Realistic and achievable objectives are set to guide the research project. Fundamental studies and further literature review on reforming technologies are done. The three types of reforming technologies focused on were steam methane reforming (SMR), partial oxidation (POX) and auto thermal reforming (ATR). In parallel with literature review, process simulation is done using HYSYS for all the three different type of reforming process to produce 1 mol/s of hydrogen. Optimum operating conditions for each type of reforming is identified. Material and energy balance is done to identify the reforming method having the lowest energy cost. Apart from that, plant data is also used for process simulation and its results are compared with the initial simulation. Percentage of error is also determined to obtain the deviation between the process simulation output and actual plant output. After finalizing the results, dissertation is prepared for submission. The project flow is described in Figure 3.1.

3.2 PROJECT WORK

The project work for this research can be divided into three which is comparative studies of three types of reforming namely SMR, POX and ATR, process simulation for all three types of reforming at its optimum operating conditions and determination of process simulation accuracy by inputting plant data.

3.2.1 Comparative Studies

Comparative study among the three different reforming technologies, steam methane reforming, partial oxidation and auto thermal reforming is done by literature review. The differences of each reforming technology are noted down. For example, the importance of steam to carbon ratio for steam methane reforming, air ratio for partial oxidation and both steam to carbon ratio and air ratio for auto thermal reforming. Other differences like reactions taking place in each reforming reactor, usual operating temperature and pressure and its energy requirements are taken into account.

3.2.2 Process Simulation

For the purpose of this research, process simulation was done using the software, Hyprotech HYSYS version 3.1. This software was chosen for process simulation as similar research has been done using AspenPlus^{TM}. Furthermore, HYSYS software is easily accessible for Universiti Teknologi Petronas students.

The process simulation for all the three reforming methods is done on basis to produce 1 mol/s of hydrogen. Other parameters steam to carbon ratio and air ratio is varied to ensure the process is operating at its optimum operating conditions to produce 1 mol/s of hydrogen by trial and error. Trial and error method was chosen, as there is literature source available to be used as a basis for determining of the operating conditions. If there was no such source, iteration should be done.

The unit operations involved in process simulation for steam methane reforming are two steam generators, two heat exchangers and two reactors. The first steam generator is used to generate steam via water to be mixed with methane. An energy stream is connected to the heater for this purpose. Both methane and steam are mixed in the mixing chamber or mixer. The feed is then preheated using the first heat exchanger. In the process simulation, a heater connected with an energy stream represents heat exchanger. The energy requirement to preheat the feed to certain temperature is necessary to be identified. The heat source and its characteristics are not important and therefore a heater is used in the simulation.

The type of reactor used for process simulation is Gibbs reactor. Gibbs reactor works on the principle of minimizing the Gibbs free energy of reaction to reach equilibrium. This is ideal for process simulation as all the reactions are assumed to be in equilibrium state. Simulation can be run using Gibbs reactor without entering the reaction mechanism. However, to increase the accuracy of simulation, the equilibrium reaction sets are specified. For steam methane reforming, the reactions specified are reforming reaction, water gas shift reaction and Boudouard reaction (below), which is where coke is formed.

$$2CO \longrightarrow C + CO_2$$

Equilibrium constant, K values can be obtained from simulation using Gibbs reactor. This constant value is used to repeat the process simulation, this time using the equilibrium reactor. Theoretically, the values obtained from process simulation using Gibbs reactor and equilibrium reactor should be the same.

For steam methane reforming methane, an energy stream is connected to the reactor. The reaction occurring in the steam methane reforming reactor is endothermic. Therefore, there is a need for continuous and sufficient heat transfer to the SMR reactor to sustain the catalytic reaction. The reforming reactor has two outlet streams, top and bottom. The synthesis gas exits from the top of the reactor while the other stream at the bottom is connected to satisfy the requirements of Gibbs reactor. Eventually, no molar flow rate is detected at the bottom of the reactor after simulation. The process gas exiting the reforming reactor is cooled down by a heat exchanger. The cold stream in the shell side is water. The exiting process gas is mixed with steam again in the second mixer. The steam supplied is generated by the second steam generator, which is represented by a heater. The outlet of mixer is connected to the water gas shift reactor, where Gibbs reactor is also used. The water gas shift reaction occurring in the reactor is exothermic. Therefore, an energy stream is connected to the reactor to transfer the heat generated from the reaction. The product exiting the shift conversion reactor is the product where the compositions are measured to determine the conversion and yield of reforming process.

Similar process simulation is done for the other two reforming methods, which are partial oxidation and auto thermal reforming. One of the differences for partial oxidation reforming is that air is mixed with methane instead of steam. For auto thermal reforming, both air and steam streams are used. Both partial oxidation and auto thermal reformers are simulated at adiabatic conditions where there is no heat transfer to or from the reactor. The process flow diagram of process simulation can be observed at figure 3.2, 3.3 and 3.4.

Table 3.1: Reactions and equilibrium constant values for process simulation

Reforming Method	Steam-Methane Reforming (SMR)	Partial Oxidation (POX)	Auto Thermal Reforming (ATR)
Reactions	i. Reforming reaction $CH_4 + H_2O \leftrightarrow 3H_2 + CO$ K @ 800°C = 192.3 ii. Shift reaction at reforming reactor $CO + H_2O \leftrightarrow H_2 + CO_2$ K @ 800°C = 1.037 iii.Shift reaction at shift reactor $CO + H_2O \leftrightarrow H_2 + CO_2$ K @ 200°C = 252.5	i. Partial oxidation $CH_4 + ½O_2 \leftrightarrow 2H_2 + CO$ ii. Shift reaction at reforming reactor $CO + H_2O \leftrightarrow H_2 + CO_2$ K @ 800°C = 1.037 iii.Shift reaction at shift reactor $CO + H_2O \leftrightarrow H_2 + CO_2$ K @ 200°C = 252.5	i. Reforming reaction $CH_4 + H_2O \leftrightarrow 3H_2 + CO$ K @ 800°C = 192.3 ii. Partial oxidation $CH_4 + ½O_2 \leftrightarrow 2H_2 + CO$ iii.Shift reaction at reforming reactor $CO + H_2O \leftrightarrow H_2 + CO_2$ K @ 800°C = 1.037 iv.Shift reaction at shift reactor $CO + H_2O \leftrightarrow H_2 + CO_2$ K @ 200°C = 252.5

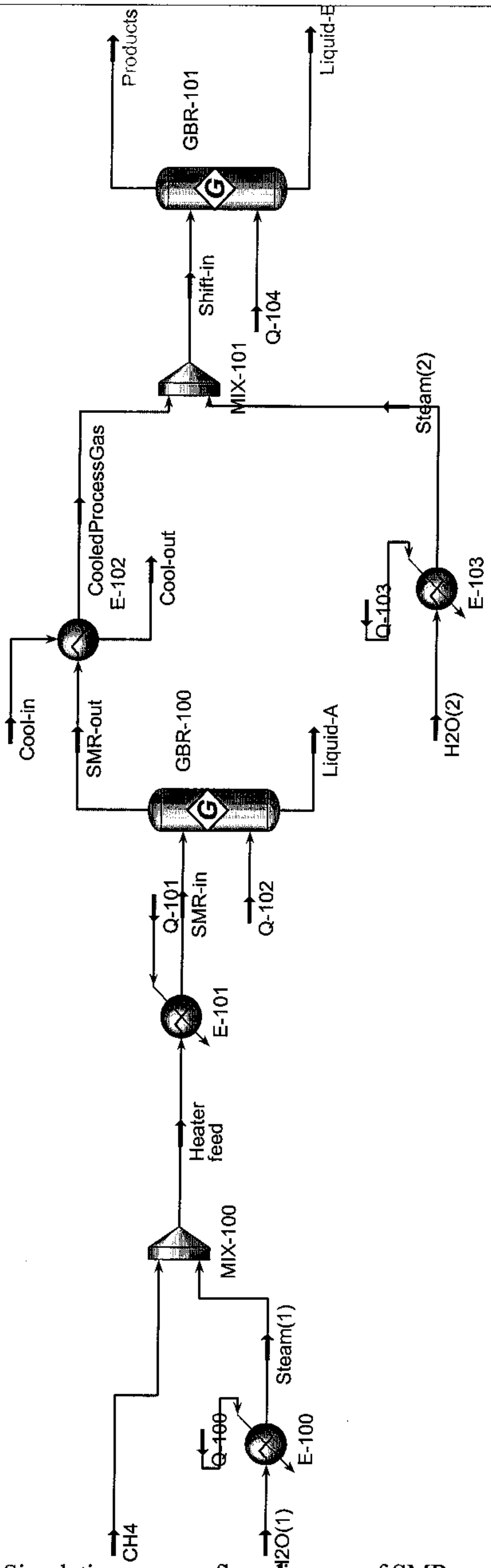


Figure 3.2: Simulation process flow diagram of SMR

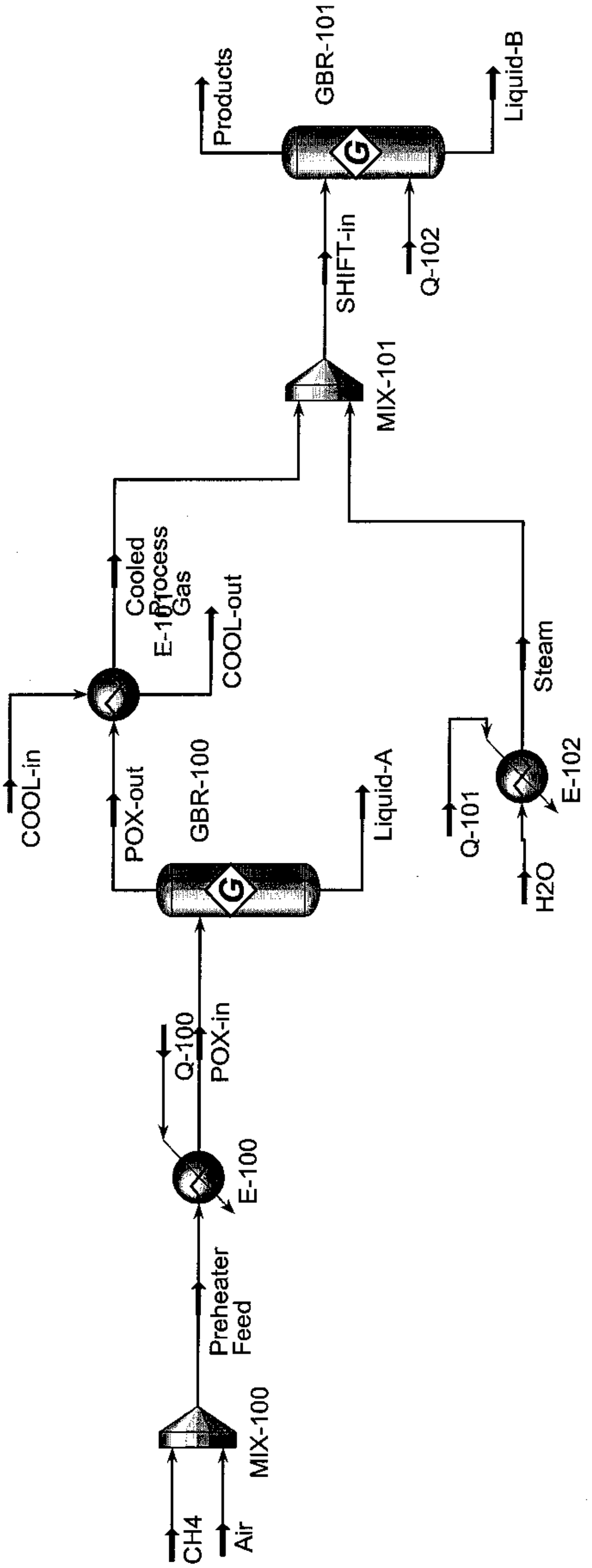


Figure 3.3: Simulation process flow diagram of POX

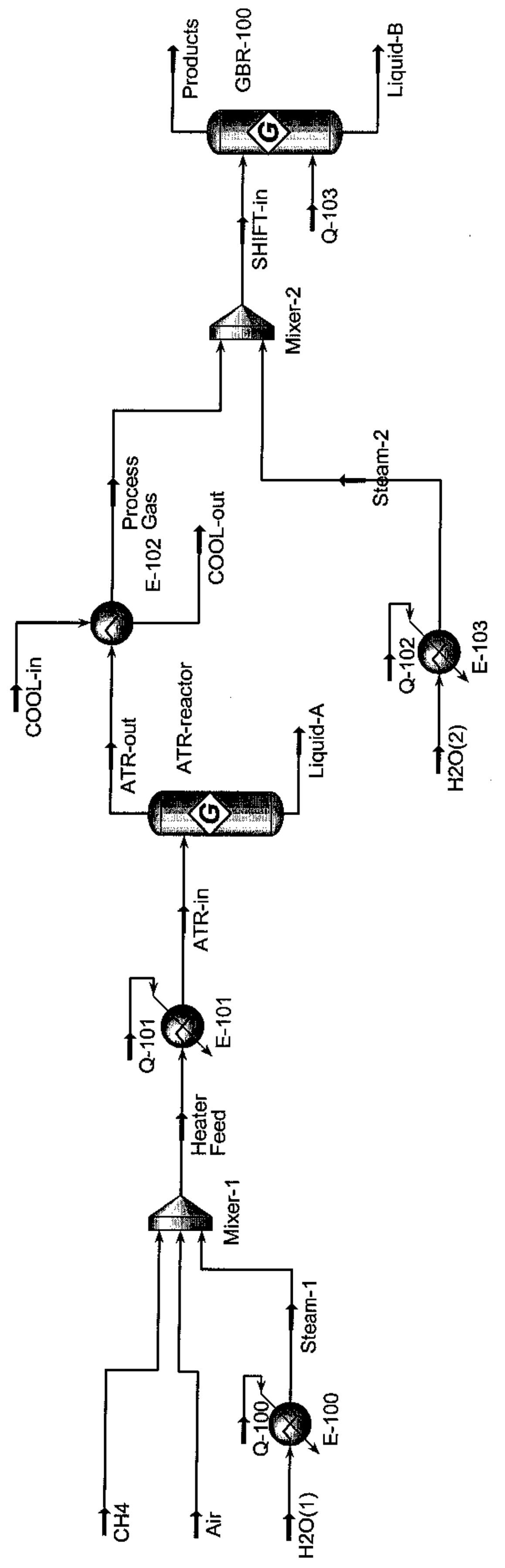


Figure 3.4: Simulation process flow diagram of ATR

3.2.3 Case Study: Process Simulation using Plant Data

Process simulation using data from a hydrogen generating plant was done to check the accuracy and reliability of simulation of HYSYS. The simulation results of three different types of reforming methods will be justified if the percentage of error between the simulation and actual plant data is minimum.

In this case, the plant data was obtained from a hydrogen generating plant in Pan Century Edible Oils Sdn. Bhd. Pan Century Edible Oils Sdn. Bhd. is one of the companies in the Aditya Birla Group. The main focus of this company is palm oil refining, oleochemicals and soap noodle manufacturing. A hydrogen generating plant also operates at the company to cater for hydrogen demand for hydrogenation process. The type of reforming method used in the company is steam methane reforming. Table 3.1 refers to the data obtained from the hydrogen generating plant.

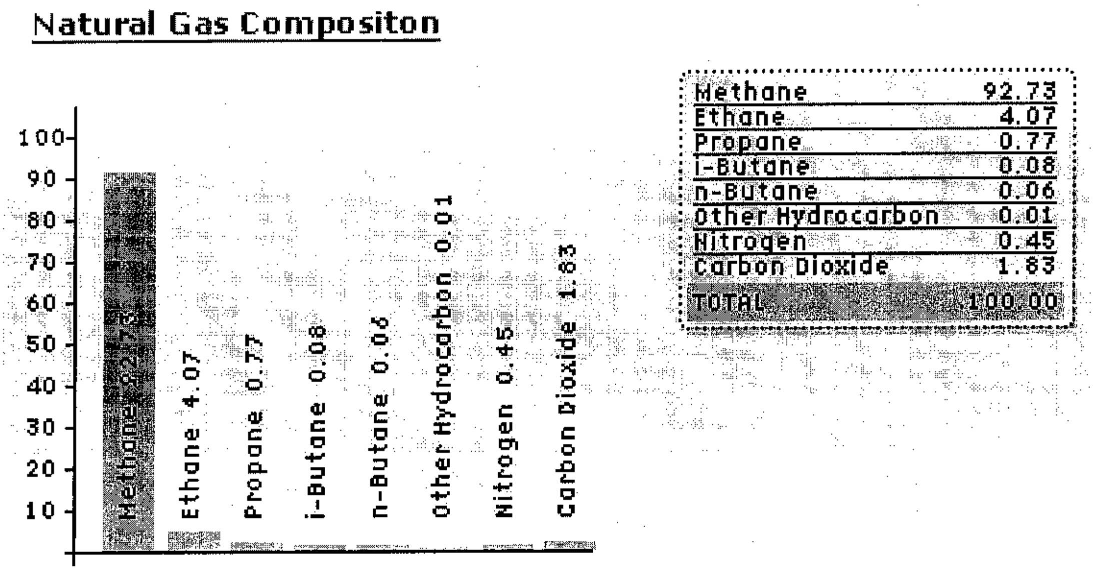
Table 3.2: Data of the steam methane reforming plant

	Description	Value
Flowrate	Natural gas to catalyst tubes	200 m^3/ hr (normal[1])
	Steam to catalyst tubes	1040kg/m^3
	N. Gas to burner/furnace	1600 m^3/hr (normal)
	Hydrogen product	600 m^3/hr (normal)
Temperature(°C)	Reformer Body	900-950
	Reformer Top	1010
	Waste Heat B inlet	982
	Waste Heat B outlet	873
	Economizer Inlet	271
	Economizer outlet	177
	Reformer Process outlet	800
	Quench Pot bottom	415
	High Temp. Shift inlet	335
	High Temp. Shift outlet	409
Pressure (barg)	Cooling Water supply	3
	Air supply	5.6
	Hydrogen back pressure	14.5
	Steam to catalyst tubes	17
	Venting Gas	0.3-0.8
	Reformer draft	6.4

---

[1] Normal condition at P=1 atm and T=15°C

Data above, which is obtained from the plant, is used for process simulation and the results of simulation will be checked as to whether the process produces the specified yield of product. The feed used is natural gas. Taking into account the main component of natural gas, the simulation requires the composition of methane. The actual composition of methane is obtained from the supplier of natural gas to the plant, Gas Malaysia Sdn. Bhd. Figure 3.5 indicates the general composition of natural gas supplied to industry by Gas Malaysia Sdn. Bhd.



Methane	92.73
Ethane	4.07
Propane	0.77
i-Butane	0.08
n-Butane	0.06
Other Hydrocarbon	0.01
Nitrogen	0.45
Carbon Dioxide	1.83
TOTAL	100.00

Figure 3.5: Composition of natural gas (Source: Gas Malaysia Sdn. Bhd. accessed 24th April 2004)

CHAPTER 4

RESULTS AND DISCUSSION

This chapter explains the results obtained from the research project. The results can be divided into three parts which are identification of optimum operating conditions, material and energy balance to identify the reforming method which has the lowest cost in terms of CH_4 equivalent to produce 1 mol/s of hydrogen and comparison between the process simulation results and plant data. The optimum conditions for steam methane reforming (SMR) is at steam to carbon ratio (S:C) of 1.9 and reactor temperature of 800°C. For partial oxidation, the optimum air ratio is 0.3 and optimum preheat temperature is 311°C. The optimum conditions for auto thermal reforming (ATR) has been identified at air ratio of 0.3, S:C of 0.35 and preheat temperature of 340°C. Preheat temperature affects the equilibrium compositions of reactor of POX and ATR as both the reactors are adiabatic. Energy balance concludes that POX has the lowest energy cost in terms of CH_4 equivalent of 0.3646 mol/s, followed by ATR and SMR. Process simulation results are then compared with the actual data obtained from industry.

4.1 OPTIMUM OPERATING CONDITIONS

During process simulation, certain parameters like steam to carbon ratio, air ratio, preheat temperature and reactor temperature are varied to identify the optimum operating conditions for methane conversion of 99%. This is done for all three reforming methods, steam methane reforming, partial oxidation and auto thermal reforming. At first simulation is done using Gibbs reactor. Using the equilibrium constant, K values obtained, it is entered into the equilibrium reactor and re-simulated.

The output results of both simulations using different reactors appear to be almost identical. Therefore, the use of Gibbs reactor here is justified.

4.1.1 Steam Methane Reforming (SMR)

The parameters varied for steam methane reforming process are the steam to carbon ratio and reactor temperature. As the steam to carbon is varied, the reactor temperature is kept constant at 800°C. This maximum temperature was chosen as increasing the temperature more will damage the thermal durability of catalysts. When the S:C ratio is varied from 0.5 to 3.0, it can be observed that the methane conversion increases from 49% to 99.7%. This proves that conversion increases as the steam to carbon ratio is increased. As steam molar flow rate increases, the amount of methane reacting with steam increases to maintain the equilibrium and therefore more products are produced. Amount of unconverted methane reduces significantly as a result of conversion increase. At a steam to carbon ratio of 1.9, it can be seen that the methane conversion reaches 99%. After that, the increase in conversion is not as much. Therefore, steam to carbon ratio above 1.9 cannot be justified in terms of methane conversion. Steam to carbon ratio of 1.9 is selected as the optimum condition for steam methane reforming (refer Figure 4.1)

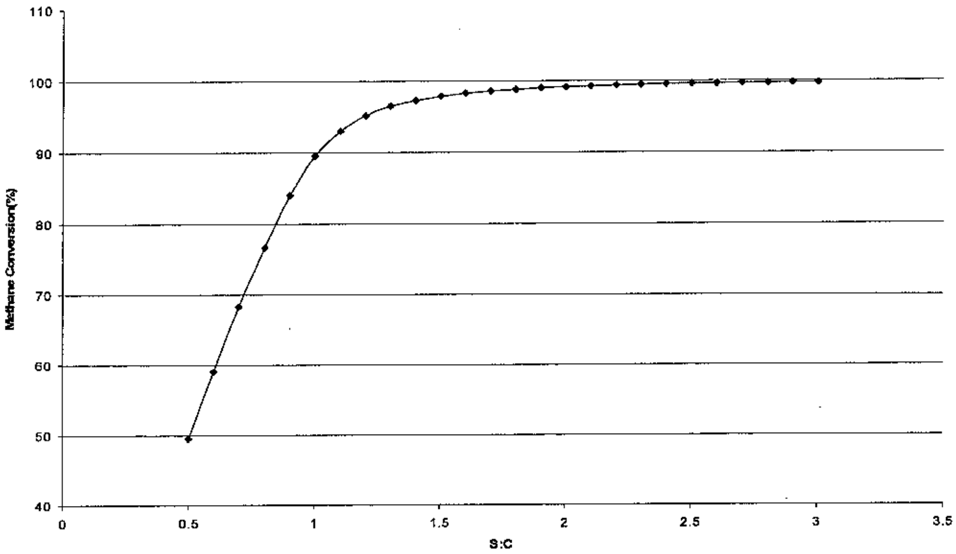


Figure 4.1: Graph of methane conversion (%) against S:C at equilibrium compositions for steam methane reforming (SMR)

As steam to carbon ratio increases, the yield of hydrogen is also found to be increasing. More hydrogen is produced as a result of steam addition which will cause the reaction to move forward. The molar flow rate of H_2O is minimum at S:C of 1.0. The water flow rate first decreases when S:C is increased and later increases when S:C is more than 1.0. Molar flow rate of carbon dioxide increases but the rate of increase becomes less when S:C is increased to more than 1.0. Molar flow rate of carbon monoxide is found to be at maximum at S:C of 1.1. Thereafter, the yield of carbon monoxide decreases. Production rate of carbon monoxide decreases as the rate of increase in conversion decreases over increasing S:C. Therefore, the formation of carbon dioxide also decreases as there is less carbon monoxide reacting with steam during the water gas shift reaction. As a result, the production of H_2O also increases. Although the rate of water gas shift reaction decreases, it is still higher than the production of carbon monoxide from the reforming reaction, which causes the yield of carbon monoxide to decrease when S:C is increased more than 1.1. As the desired product in this case is hydrogen, the decrease of carbon monoxide production is not as important. From the simulation results, steam to carbon ratio of 1.9 for a conversion of 99% is justified. Figure 4.2 and 4.3 shows the product flow rate against increasing steam to carbon ratio (S:C).

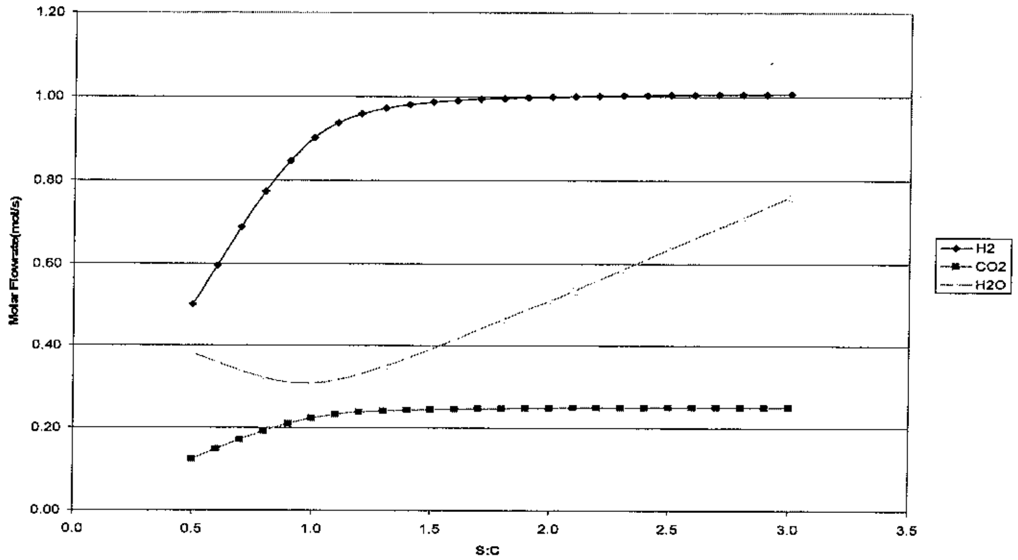


Figure 4.2: Graph of product molar flow rate (mol/s) (H_2, CO_2, H_2O) against S:C at equilibrium compositions for steam methane reforming (SMR)

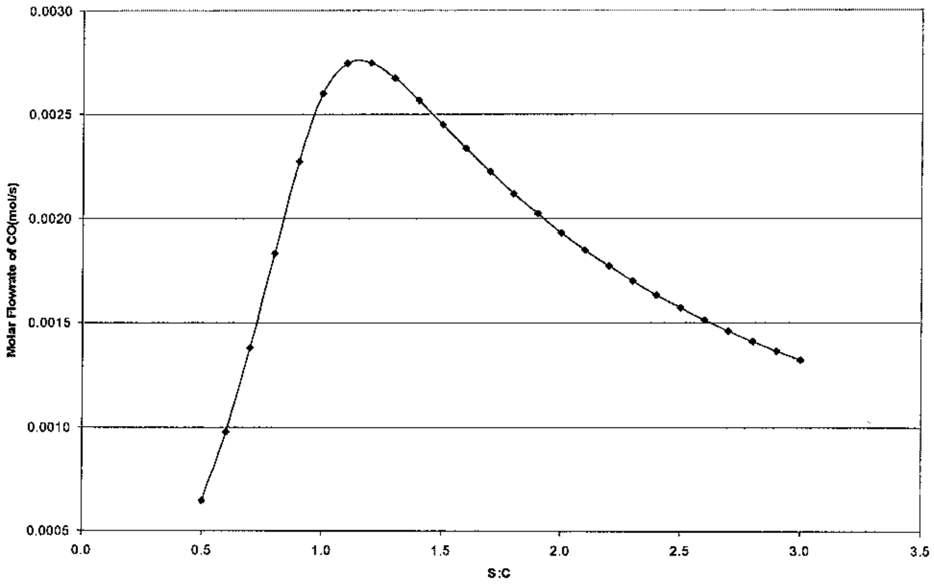


Figure 4.3: Graph of product molar flow rate (mol/s) (CO) against S:C at equilibrium compositions for steam methane reforming (SMR)

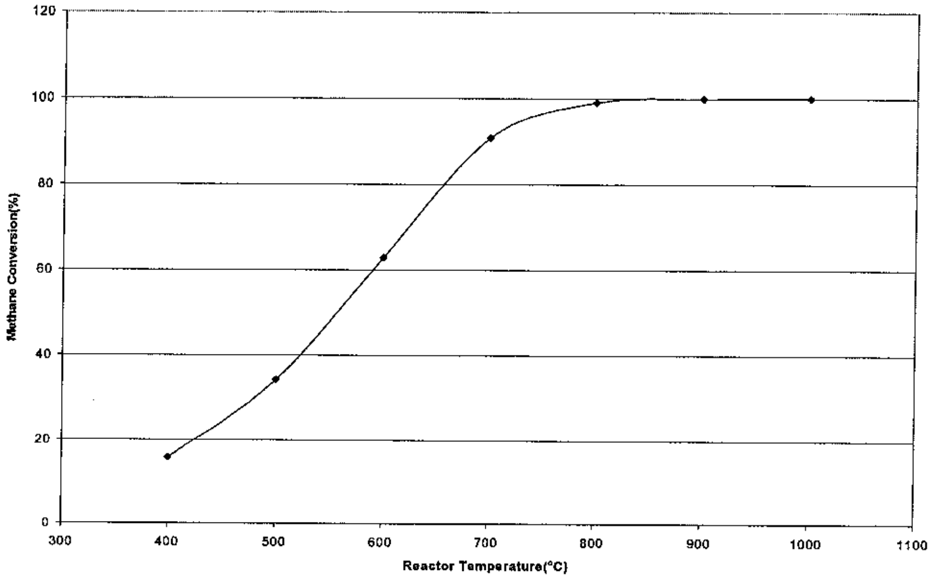


Figure 4.4: Graph of methane conversion (%) against reactor temperature (°C) at equilibrium compositions for steam methane reforming (SMR)

Methane conversion also increases as reactor temperature increases with the steam to carbon ratio kept constant (refer figure 4.4). With a S:C of 1.9, the reactor temperature of 800°C gives a methane conversion of 99%. Increasing the reactor temperature above 800°C to give a 100% conversion is not advisable as the thermal durability of catalysts could be damaged. An increase of 1% in conversion cannot be justified if the catalyst beds have to be changed frequently as a result of catalyst deactivation. As the reactor temperature increases, the production of synthesis gas (H_2 and CO) also significantly increases. Increase in reaction temperature increases the rate of reaction in the reforming reactor. Increase in carbon monoxide yield also causes the water gas shift reaction rate to increase. As a result, the carbon dioxide molar flow rate increases while steam flow rate decreases. Figure 4.5 and 4.6 shows the product flow rate against increasing reactor temperature. The simulation worksheet for steam methane reforming at optimum operating conditions can be referred at Appendix A-1.

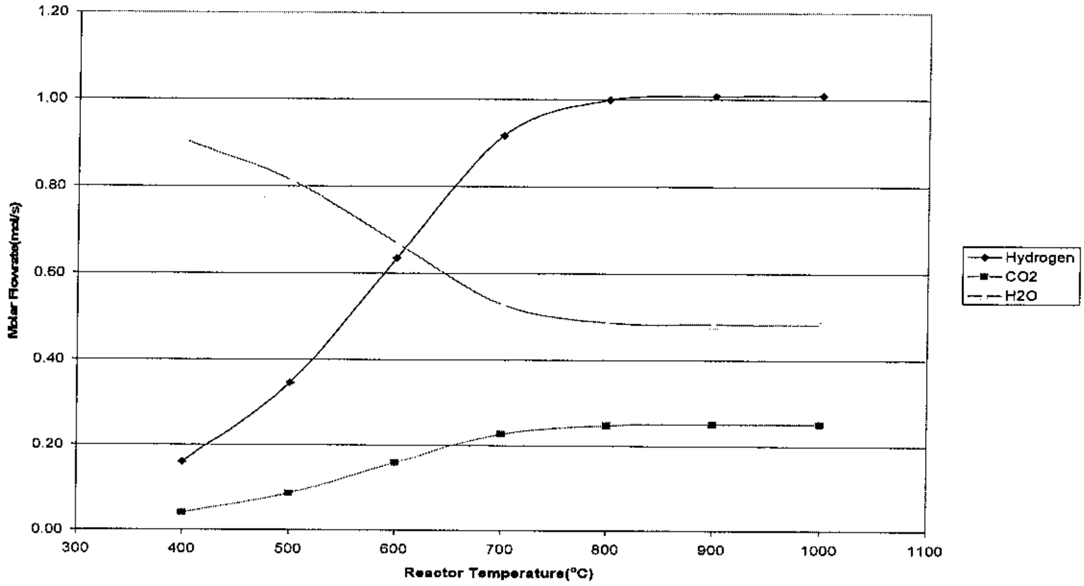


Figure 4.5: Graph of product molar flow rate (mol/s) (H_2, CO_2, H_2O) against reactor temperature (°C) at equilibrium compositions for steam methane reforming (SMR)

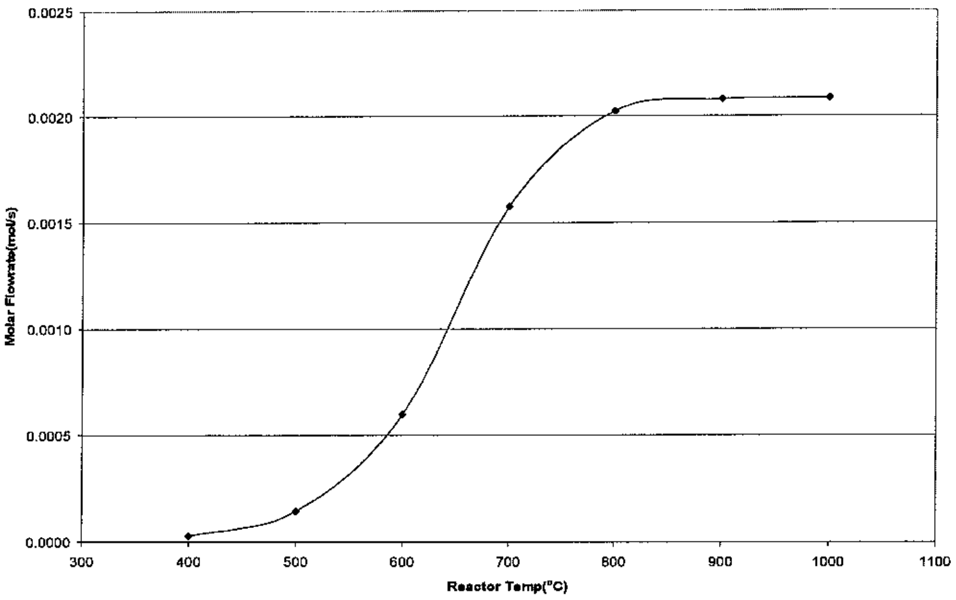


Figure 4.6: Graph of product molar flow rate (mol/s) (CO) against reactor temperature (°C) at equilibrium compositions for steam methane reforming (SMR)

4.1.2 Partial Oxidation (POX)

For the process simulation of partial oxidation reforming, parameters varied were the preheat temperature and air ratio. The preheat temperature is varied as the reforming reactor is simulated at adiabatic condition. As the air ratio increases, the methane conversion is also observed to be increasing. While air ratio is increased, the preheat temperature is kept constant. The reactions are also assumed to be in equilibrium. Methane conversion is around 99% at the air ratio of 0.3 (refer figure 4.7). The molar flow rate of oxygen reacting with methane to produce synthesis gas is linearly related to air ratio. As air ratio is increased, amount of reactant increases causing a forward reaction to produce more products. More methane is reacted, which decreases the molar flow rate of unconverted methane.

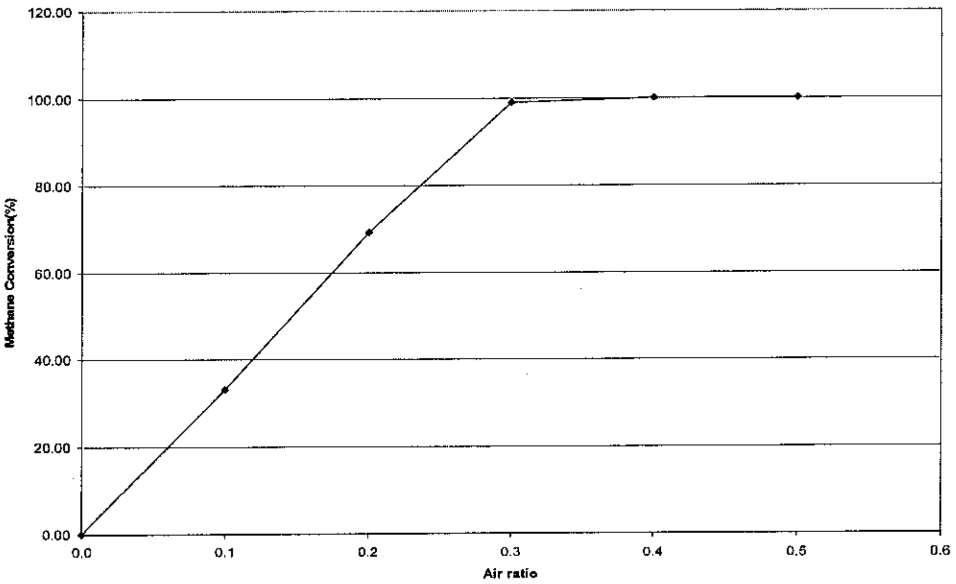


Figure 4.7: Graph of methane conversion (%) against air ratio at equilibrium compositions for partial oxidation reforming (POX)

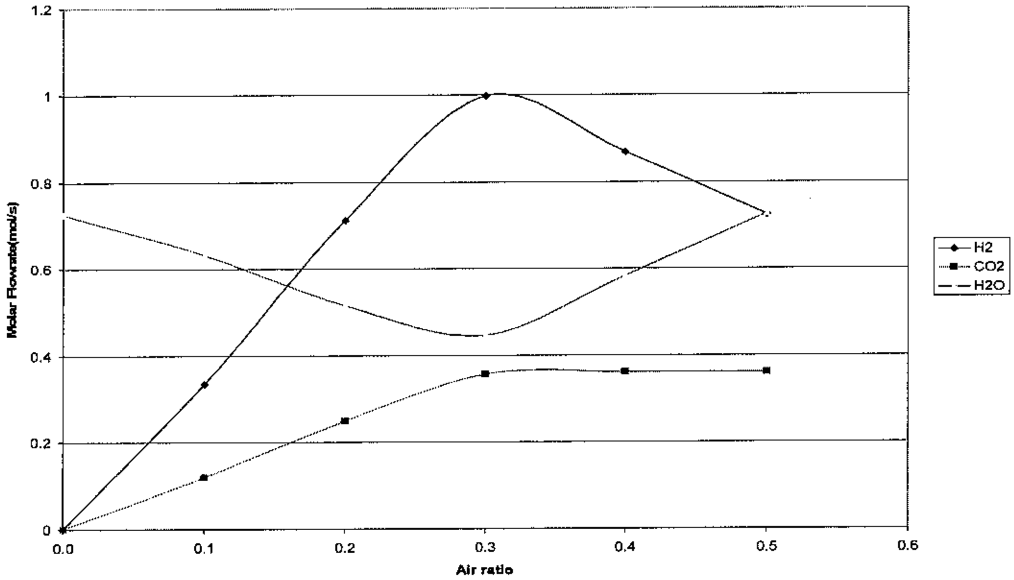


Figure 4.8: Graph of product molar flow rate (mol/s) (H_2, CO_2, H_2O) against air ratio at equilibrium compositions for partial oxidation reforming (POX)

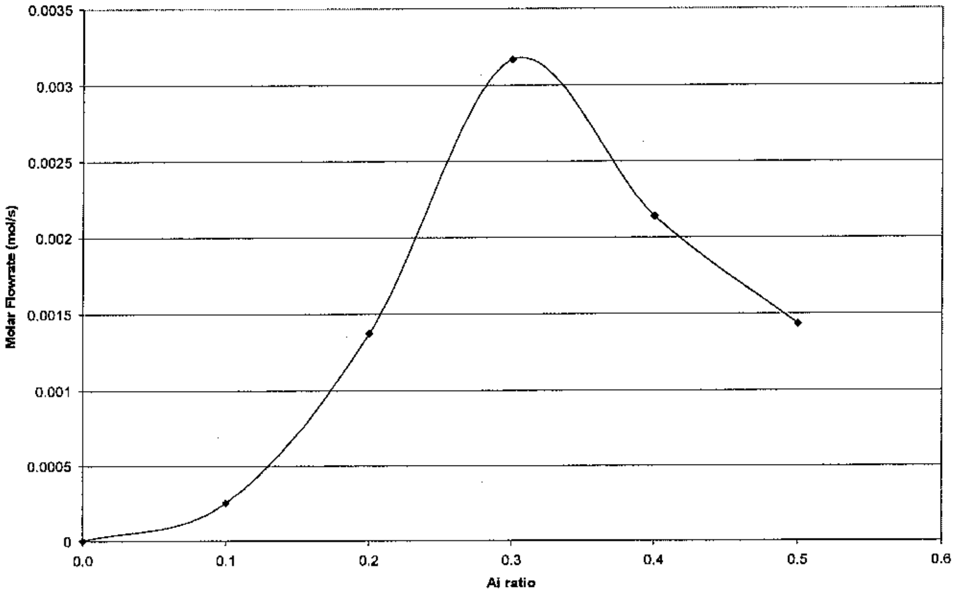


Figure 4.9: Graph of product molar flow rate (mol/s) (CO) against air ratio at equilibrium compositions for partial oxidation reforming (POX)

The molar flow rate of hydrogen increases when air ratio is increased from 0.0 to 0.3. Thereafter, the hydrogen flow rate decreases. Extensive supply of oxygen oxidizes the hydrogen produced from reforming to produce steam. Figure 4.8 shows that steam flow rate increases when air ratio is above 0.3, concurrently with decrease in hydrogen production. Based on the figure 4.9, carbon monoxide yield also reduces when air ratio is above 0.3 as excess O_2 oxidizes the carbon monoxide to produce carbon dioxide. Based on the results, air ratio of 0.3 is justified as higher air ratio could be detrimental to the main purpose of producing hydrogen.

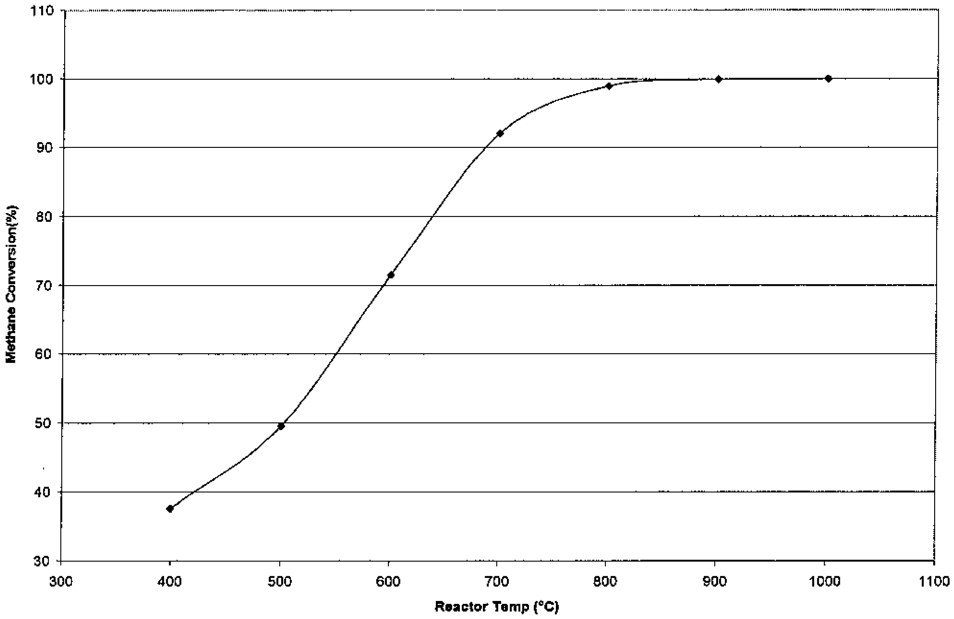


Figure 4.10: Graph of methane conversion (%) against reactor temperature (°C) at equilibrium compositions for partial oxidation reforming (POX)

Figure 4.10 shows that increasing the temperature above 800°C does not increase the conversion much. This simulation is done at a constant air ratio of 0.3 to prove the effect of increasing reactor temperature to the methane conversion. However, in this case, the reactor temperature is kept constant at 800°C as it is adiabatic.

Increasing the preheat temperature also increases the conversion. As the reactor is adiabatic, any change in preheat temperature will also affect the operating temperature of reactor, hence the equilibrium compositions in reactor. This can be observed in figure 4.11, 4.12, and 4.13. However, the effect on increasing preheat temperature is not as critical as of reactor temperature. This is because there is an increase of temperature in reactor as a result of exothermic reaction and therefore the impact of preheat temperature is not as big as increase in temperature as a result of reaction. The simulation worksheet for partial oxidation reforming at optimum operating conditions can be referred at Appendix A-2.

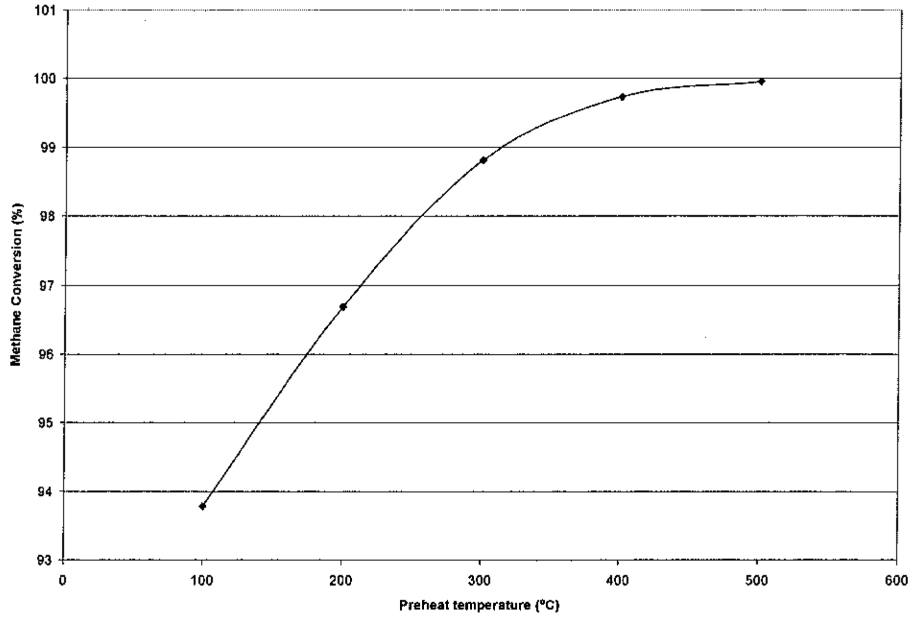


Figure 4.11: Graph of methane conversion (%) against preheat temperature (°C) at equilibrium compositions for partial oxidation reforming (POX)

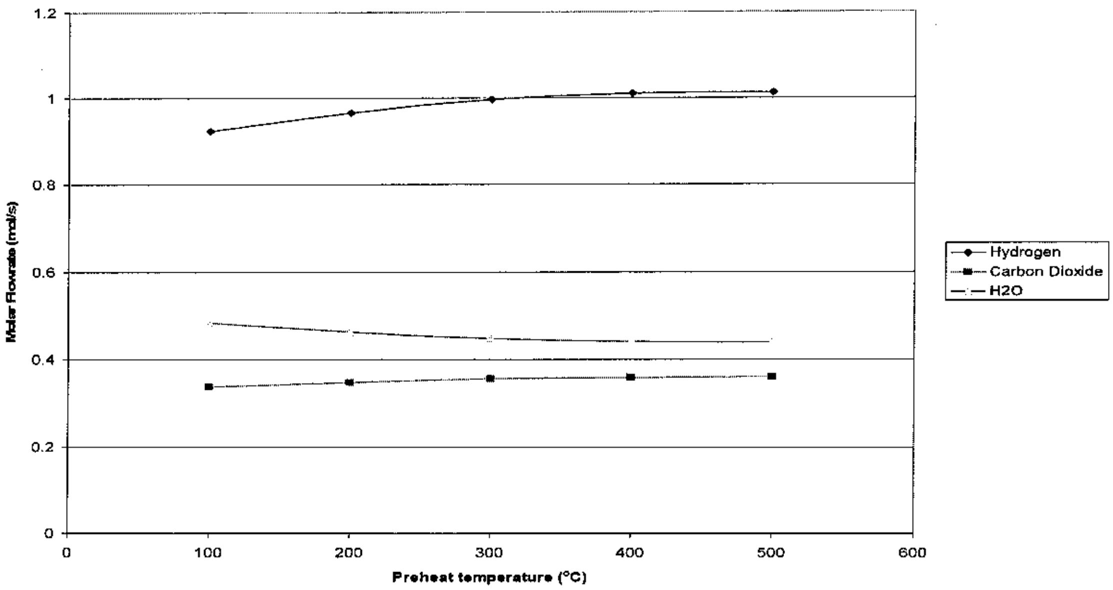


Figure 4.12: Graph of product molar flow rate(mol/s) (H_2, H_2O, CO_2) against preheat temperature (°C) at constant air ratio of 0.3

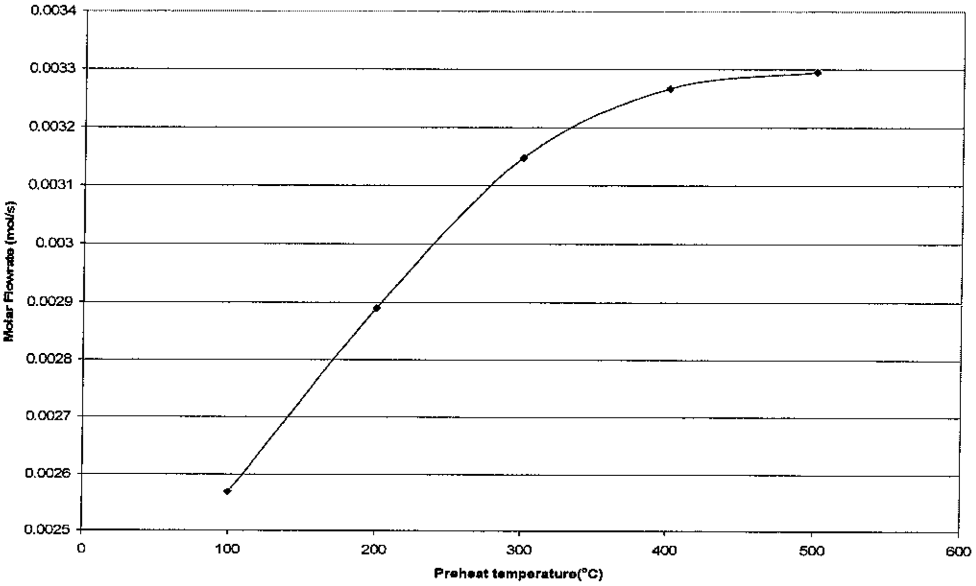


Figure 4.13: Graph of product molar flow rate (mol/s) (CO) against preheat temperature (°C) at constant air ratio of 0.3

4.1.3 Auto Thermal Reforming (ATR)

Process of identifying the optimum operating conditions for auto thermal reforming involves varying parameters such as air ratio, steam to carbon ratio and preheat temperature. The air ratio is varied at different steam to carbon ratio to identify its effect on the conversion and product yield. Based on figure 4.14, it can be observed that as the air ratio increases, conversion of methane increases. When air ratio is increased for systems with different steam to carbon ratio, the system with a higher steam to carbon ratio gives a lower conversion. In an auto thermal reforming reactor, two types of reforming reactions take place, steam reforming and partial oxidation. Steam reforming reaction is endothermic while methane oxidation is exothermic. Unlike steam methane reforming which has a continuous heat supply to raise the temperature of reaction, the auto thermal reactor is simulated at adiabatic condition. At constant air ratio, the rate of methane oxidation is constant. Therefore, the heat generated from the exothermic reaction is also constant. As steam to carbon ratio increases, more heat is needed to sustain the endothermic reaction. Thus, more heat is absorbed by the endothermic reaction which will eventually cause the reactor temperature to decrease. As the reactor temperature decreases, the overall conversion decreases.

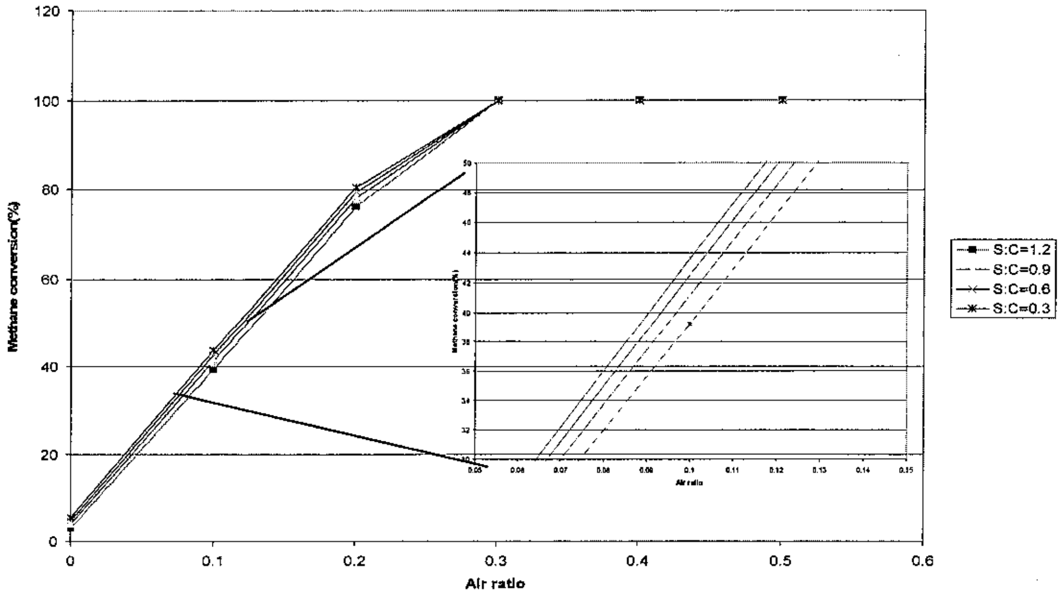


Figure 4.14: Graph of methane conversion (%) against air ratio for auto thermal reforming (ATR)

As air ratio increases, the yield of hydrogen increases as steam to carbon ratio increases (refer figure 4.15) but the yield of carbon monoxide decreases (refer figure 4.16). The carbon monoxide production decreases as more steam could cause water gas shift reaction rate to increase and produce more carbon dioxide. The hydrogen production rate decreases after an air ratio of 0.3 as hydrogen is oxidized as a result of excess oxygen in system. Similarly, carbon monoxide yield also decreases when air ratio is more than 0.3, which results from the oxidation of carbon monoxide to form carbon dioxide. However, the hydrogen molar flow rate drops more steeply when compared to the decrease in carbon monoxide molar flow rate. This is due to the faster oxidation of hydrogen than carbon monoxide in the region of higher air ratio.

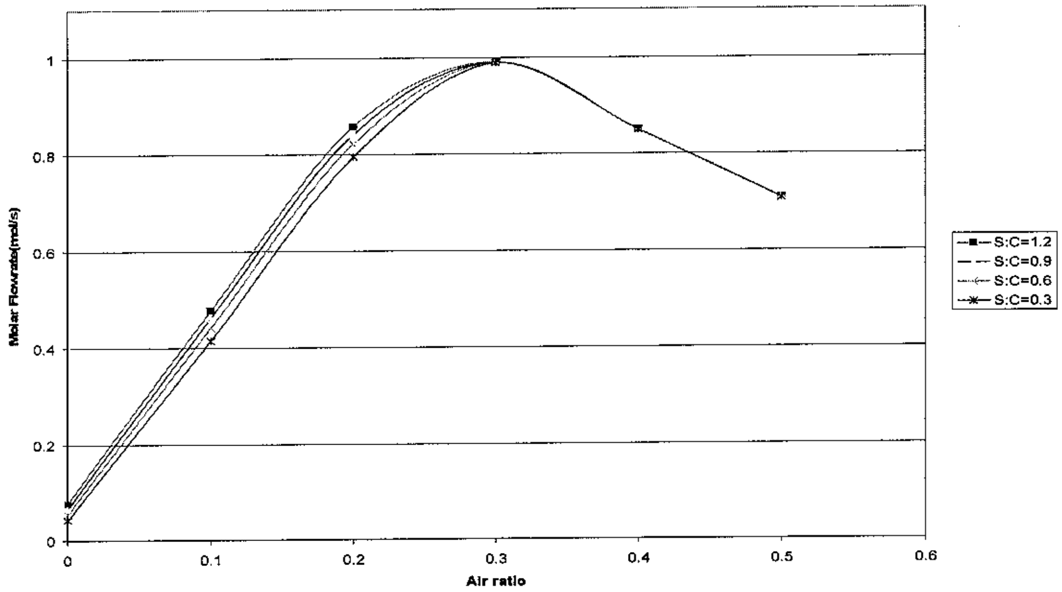


Figure 4.15: Graph of hydrogen molar flow rate (mol/s) against air ratio at equilibrium compositions for auto thermal reforming (ATR)

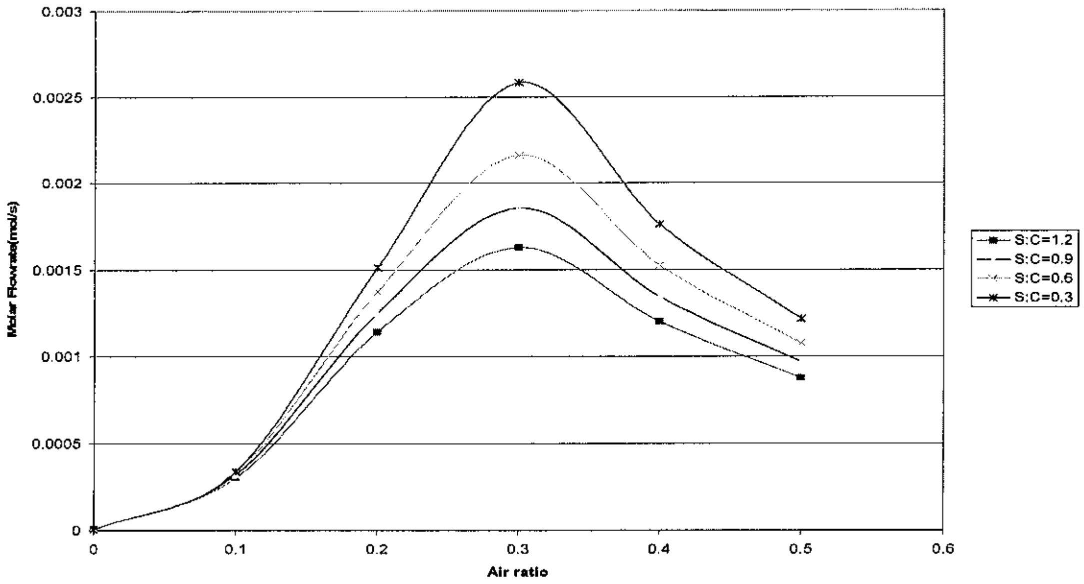


Figure 4.16: Graph of CO molar flow rate (mol/s) against air ratio at equilibrium compositions for auto thermal reforming (ATR)

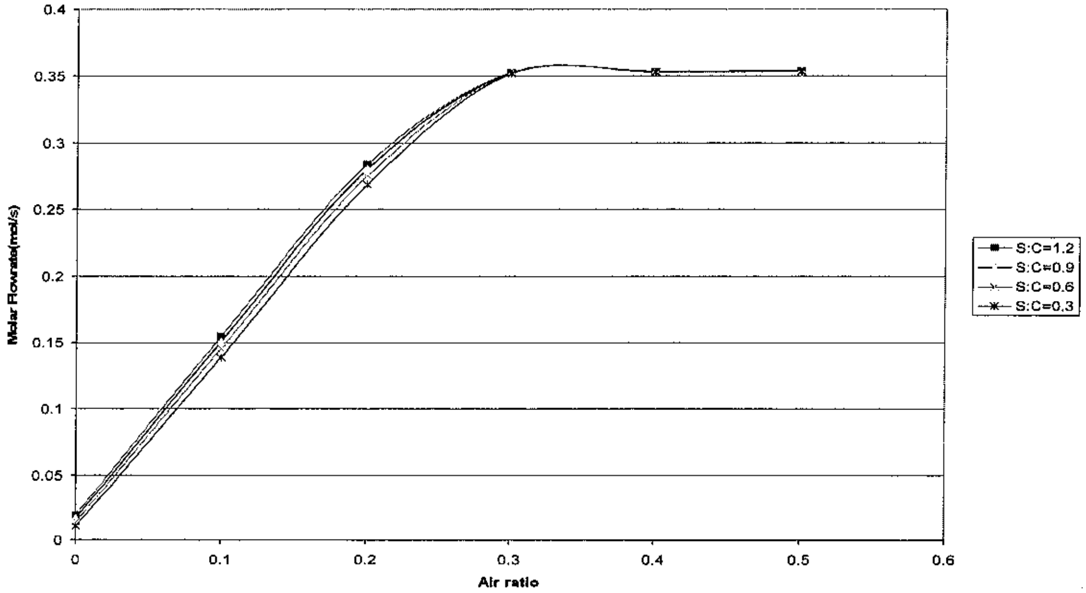


Figure 4.17: Graph of CO_2 molar flow rate (mol/s) against air ratio at equilibrium compositions for auto thermal reforming (ATR)

Based on figure 4.17, CO_2 increases as air ratio increases as oxidation rate increases. At constant air ratio and increasing S:C, CO_2 flow rate also increases as a result of increase in water gas shift reaction. Steam flow rate at first decreases when air ratio is increased but later increases when air ratio is more than 0.3 (refer figure 4.18). This is due to the oxidation of hydrogen to produce H_2O. Amount of steam flowing out from a system with a high S:C is higher than the one with a low S:C simply because there is more steam in the system. When preheat temperature is increased, the conversion and product yield of ATR process increases. The behaviour of system towards the change in preheat temperature is similar to partial oxidation reforming. The results of variation in preheat temperature can be referred in Appendix B-1 and B-2. The simulation worksheet for auto thermal reforming at optimum operating conditions can be referred at Appendix A-3.

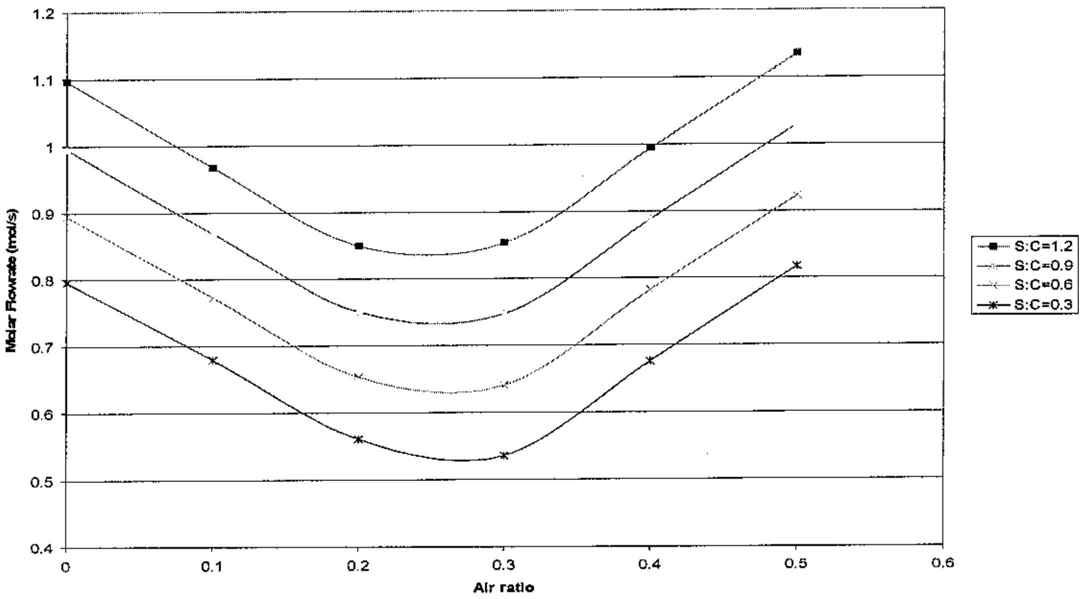


Figure 4.18: Graph of H_2O molar flow rate (mol/s) against air ratio at equilibrium compositions for auto thermal reforming (ATR)

4.2 MATERIAL AND ENERGY BALANCE

The output of process simulation with the optimum operating conditions is used to produce material and energy balance. The balance is done to identify the reforming method which has the lowest energy cost in terms of CH_4 equivalent to produce 1 mol/s of hydrogen. The process is simulated to produce 1 mol/s of hydrogen.

For the material balance, molar flow rates of components fed and exiting the reforming system are listed. For steam methane reforming, flow rates of O_2 and N_2 do not exist as air is not fed into the system. In the case of POX, there is no input of steam to the reforming reactor. However, steam is supplied to the shift reactor. Mol fraction of O_2 and N_2 in air is taken to be 0.2095 and 0.7905 respectively. The input and output of nitrogen for POX and ATR does not change as nitrogen is inert. The CH_4 conversion and CO conversion are calculated.

$$\text{Methane Conversion} = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \; x \;\; 100\%$$

$$\text{Carbon Monoxide Conversion in shift reactor} = \frac{[CO]_{in} - [CO]_{out}}{CO_{in}} \; x \;\; 100\%$$

The conversion for reforming reaction in reforming reactor and shift reaction in shift reactor is around 99% for all three reforming methods. Energy balance is made by adding if energy is consumed and subtracting if energy is being generated. The total amount obtained from balance is the amount of energy needed for the particular system. For steam methane reforming, there are six areas for energy transfer. Partial oxidation involves four areas as the reactor is adiabatic and no steam need to be generated for reforming reaction. In an auto thermal reforming system, there are five areas of heat transfer, namely two steam generating units, a heat exchanger, a preheater and a shift reactor where exothermic reaction takes place. The overall heat transfer efficiency of system is assumed to be 80%. 80% was taken to be the general heat transfer efficiency of the system based on the journal by Y.S.-Seo (2002).

From calculations, the net amount of energy needed for SMR is 118460 kW, 1282.5 kW for POX and 9817.5 for ATR. The energy is then converted into CH_4 equivalent using the heat of combustion of methane.

Heat of combustion of methane = -0.8026 x 10^6 kJ/mol
(Source: Perry's Chemical Engineers' Handbook, Seventh Edition)

$$\text{Energy in } CH_4 \text{ equivalent (mol/s)} = \frac{\text{Energy required for reforming process kW)}}{\text{Heat of combustion of methane (kJ/mol)}}$$

$$= \frac{E(kW)}{0.8026\ x\ 10^6\ kJ/mol}$$

Energy in CH_4 equivalent is totaled with the amount of CH_4 fed to the system to obtain the total energy cost of reforming in terms of CH_4. From the energy balance, POX has the lowest cost of 0.3646 mol/s of methane. ATR needs 0.3668 mol/s and SMR needs 0.4006 mol/s of methane to produce 1 mol/s of hydrogen. This shows that partial oxidation reforming has the lowest energy cost to produce the same amount of hydrogen from CH_4. Table 4.1 shows the material and energy balance done based on process simulations.

Table 4.1: Material and energy balance for at optimum operating conditions

	SMX	**POX**	**ATR**
Input (mol/s)			
CH_4	0.2526	0.363	0.3546
O_2	-	0.2178	0.2127
N_2	-	0.8218	0.8029
H_2O for reforming	0.4799	-	0.1241
H_2O for shift reaction	0.5052	0.726	0.7092
Output(mol/s)			
CH_4	0.00255	0.00374	0.000336
O_2	0	0	0
N_2	0	0.8218	0.8029
H_2O	0.487	0.44625	0.5527
CO	0.00202	0.00317	0.0025
CO_2	0.2480	0.3561	0.3518
H_2	0.9982	0.9983	0.9891
CH_4 conversion(%)	99.0	99.8	99.9
CO conversion(%)	99.0	99.0	99.2
Energy Balance (kW)			
Preheater	9483	13630	20250
Reforming reactor	68930	0	0
Heat exchanger	-22128	-33444	-39556
Shift reactor	-8177	-13550	-12240
Steam generator for reforming	22730	0	5880
Steam generator for shift reaction	23930	34390	33520
Energy required for reforming system (kW)	94768	1026	7854
Heat transfer efficiency	0.8	0.8	0.8
Net energy supplied (kW)[2]	118460	1282.5	9817.5
Energy in CH_4 equivalent (mol/s)	0.148	0.0016	0.0122
CH_4 used as feed (mol/s)	0.2526	0.363	0.3546
Total CH_4(mol/s)	**0.4006**	**0.3646**	**0.3668**

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[2] *Net energy supplied = (Energy required / Heat transfer efficiency)*

4.3 COMPARISON WITH PLANT DATA

Plant data obtained from a hydrogen generating plant in industry is used for process simulation. The type of reforming involved is steam methane reforming. The flow rate of natural gas into the reforming reactor is 200 m^3/hr. Based on the natural gas obtained from Gas Malaysia Sdn. Bhd., the methane composition is around 92.73%.

Flow rate methane fed = 200 m^3/hr (normal) x 0.9273 = 185.46 m^3/hr (normal)
Using ideal gas flow at normal condition, where P=1 atm and T=15°C,

$$P\hat{V} = \hat{n}RT$$

[1 atm] [185460 liters/hr] = n x [0.08206 atm.liters/mol.K] x [288.15K]]
n = 7843.32 mol/hr = 2.18 mol/s

Flow rate of methane is used for process simulation, similar with simulations done earlier. The plant has an output of 600 m^3/hr (normal) of hydrogen gas, which is equivalent to 7.05 mol/s. Plant data is used for process simulation and it results in the production of 8.55 mol/s of hydrogen.

To compare with the process simulation done earlier, the output of process simulation should be 1 mol/s of hydrogen gas. Using the principle of material balance, a ratio is calculated to either scale up or scale down the output of plant process simulation to produce 1 mol/s of hydrogen. The scale up/down ratio is calculated by;

Scale down ratio = (8.55 mol/s) / (1 mol/s)
= 8.55

The initial feed parameters for the process simulation using plant data is divided by the scale down ratio.

Scaled down methane flow rate = 2.18 mol/s / 8.55

= 0.2550 mol/s

Scaled down steam flow rate = 11.748 mol/s / 8.55

= 1.374 mol/s

Based on Table 4.2, the amount of methane fed for reforming process to produce 1 mol/s is almost similar. In the initial process simulation, steam is fed in two areas which are the reforming reactor and the water gas shift reactor. In contrast, steam is not fed into the shift reactor in the plant. This is because excessive steam (S:C = 5.39) is fed into the reforming reactor. The molar flow rate of steam exiting the reforming system is much higher for the plant. Apart from that, the reforming plant might not have been designed for water gas shift reaction to occur and could have been modified at later stage. From Table 4.2, it can be observed that the methane conversion is higher at higher S:C. In the plant, the steam is removed via knock out drum.

Plant data process simulation worksheet can be referred at Appendix A-4

Table 4.2: Comparison of material balance between process simulation and plant data

Parameters	**SMR – simulation (S:C=1.9)**	**SMR – plant data (S:C=5.39)**
Input (mol/s)		
CH_4	0.2526	0.2550
O_2	-	-
N_2	-	-
H_2O for reforming	0.4799	1.374
H_2O for shift reaction	0.5052	-
Output(mol/s)		
CH_4	0.00255	0.00112
O_2	0	0
N_2	0	0
H_2O	0.487	0.8787
CO	0.00202	0.00843
CO_2	0.2480	0.2435
H_2	0.9982	0.999
CH_4 conversion(%)	99.0	99.6
CO conversion(%)	99.0	92.7

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

Comparative analysis have been done on the three types of reforming methods, which are steam methane reforming (SMR), partial oxidation (POX) and auto thermal reforming (ATR). The optimum steam to carbon ratio (S:C) for steam methane reforming reactor is found to be 1.9. The optimum air ratio for POX reactor is 0.3 with a preheat temperature of 311°C. The optimum air ratio and S:C ratio of the ATR reactor are 0.3 and 0.35 respectively with a preheat temperature of 340°C. The simulated mass and energy balance shows that the methane flow rates required to generate 1mol/s of hydrogen are 0.4006 mol/s for SMR, 0.3646 mol/s for POX and 0.3668 mol/s for the ATR. The balance demonstrates that partial oxidation reforming system has the lowest energy cost to produce 1 mol/s of hydrogen as compared to auto thermal reforming and steam methane reforming. The values obtained here are similar to the ones obtained by Seo.Y.-S et al. (2002). The comparison between process simulation and plant data was done. The amount of methane needed to produce 1 mol/s of hydrogen is quite similar for both sets of data. Methane conversion for the plant data is higher as a much higher S:C is used.

5.2 RECOMMENDATIONS

This study can be used as a basis to develop more detailed study and analysis on reforming technology. Mathematical modeling of processes by development of equations can be done and combined with process simulation to yield more accurate results. Modeling must include the reaction kinetics, mass transfer occurring in process and coke formation for a more accurate analysis of suitable operating conditions.

The difference in energy cost among the three reforming processes can be reduced if the heat transfer efficiency of system is high. This can be achieved by installing high efficiency heat exchangers. Thus, the difference in cost would be reduced but POX will still remain as the cheapest method. This is because the energy requirement for POX is still the lowest of all. Proper heat integration could also be done to reduce the overall energy requirement. It can be done by considering the process as a whole and can be conducted using the pinch analysis.

Rigorous plant data should also be used to analyze and be compared with the process simulation. Using more data, the comparison results will be stronger and more reliable.

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Appendix A-1

- SMR Worksheet

Workbook: Case (Main)

Streams

		CH4	H2O(1)	Steam(1)	Heater feed	SMR-in
raction		1.0000	0.0000	1.0000	0.9867	1.0000
ture	(C)	19.85 *	19.85 *	102.9 *	87.96	399.9 *
	(kPa)	100.0 *	100.0 *	100.0 *	100.0	100.0
w	(kgmole/h)	909.4 *	1728 *	1728	2637	2637
w	(kg/h)	1.459e+004	3.112e+004	3.112e+004	4.571e+004	4.571e+004
Liq Vol Flow	(m3/h)	48.73	31.19	31.19	79.91	79.91
w	(kJ/h)	-6.830e+007	-4.938e+008	-4.119e+008	-4.802e+008	-4.461e+008
thalpy	(kJ/kgmole)	-7.510e+004	-2.858e+005	-2.384e+005	-1.821e+005	-1.692e+005

		SMR-out	Liquid-A	Cool-in	Cool-out	CooledProcessGas
raction		1.0000	0.0000	0.0000	0.0000	1.0000
ture	(C)	800.0 *	800.0	19.85 *	48.32	245.4
	(kPa)	100.0	100.0	100.0 *	100.0 *	100.0 *
w	(kgmole/h)	4437	0.0000	3.600e+004 *	3.600e+004	4437
w	(kg/h)	4.571e+004	0.0000	6.485e+005	6.485e+005	4.571e+004
Liq Vol Flow	(m3/h)	130.1	0.0000	649.9	649.9	130.1
w	(kJ/h)	-1.979e+008	0.0000	-1.029e+010	-1.021e+010	-2.776e+008
thalpy	(kJ/kgmole)	-4.461e+004	-4.461e+004	-2.858e+005	-2.836e+005	-6.256e+004

		H2O(2)	Steam(2)	Shift-in	Products	Liquid-B
raction		0.0000	1.0000	1.0000	1.0000	0.0000
ture	(C)	19.85 *	102.9 *	200.0 *	200.0 *	200.0
	(kPa)	100.0 *	100.0 *	100.0	100.0	100.0
w	(kgmole/h)	1819 *	1819	6256	6256	0.0000
w	(kg/h)	3.276e+004	3.276e+004	7.848e+004	7.848e+004	0.0000
Liq Vol Flow	(m3/h)	32.83	32.83	162.9	183.7	0.0000
w	(kJ/h)	-5.198e+008	-4.336e+008	-7.113e+008	-7.407e+008	0.0000
thalpy	(kJ/kgmole)	-2.858e+005	-2.384e+005	-1.137e+005	-1.184e+005	-1.184e+005

		Q-100	Q-101	Q-102	Q-103	Q-104
raction		---	---	---	---	---
ture	(C)	---	---	---	---	---
	(kPa)	---	---	---	---	---
w	(kgmole/h)	---	---	---	---	---
w	(kg/h)	---	---	---	---	---
Liq Vol Flow	(m3/h)	---	---	---	---	---
w	(kJ/h)	8.184e+007	3.414e+007	2.481e+008	8.616e+007	-2.944e+007
thalpy	(kJ/kgmole)	---	---	---	---	---

Unit Ops

ration Name	Operation Type	Feeds	Products	Ignored	Calc. Level
	Mixer	CH4 Steam(1)	Heater feed	No	500.0 *
	Mixer	CooledProcessGas Steam(2)	Shift-in	No	500.0 *
	Heater	H2O(1) Q-100	Steam(1)	No	500.0 *
	Heater	Heater feed Q-101	SMR-in	No	500.0 *
	Heater	H2O(2) Q-103	Steam(2)	No	500.0 *
	Gibbs Reactor	Shift-in Q-104	Liquid-B Products Q-104	No	500.0 *
	Gibbs Reactor	SMR-in Q-102	Liquid-A SMR-out	No	500.0 *

* Specified by user.

Workbook: Case (Main) (continued)

Unit Ops (continued)

ration Name	Operation Type	Feeds	Products	Ignored	Calc. Level
)	Gibbs Reactor		Q-102	No	500.0 *
	Heat Exchanger	SMR-out	CooledProcessGas	No	500.0 *
		Cool-in	Cool-out		

* Specified by user.

Appendix A-2

- POX Worksheet

Workbook: Case (Main)

Streams

	CH4	Air	Preheater Feed	POX-in	POX-out
raction	1.0000	1.0000	1.0000	1.0000	1.0000
ture (C)	19.85 *	19.85 *	19.71	311.0 *	800.3
(kPa)	100.0 *	10.00 *	10.00	100.0 *	100.0
w (kgmole/h)	1307 *	3743 *	5049	5049	6852
w (kg/h)	2.096e+004	1.080e+005	1.289e+005	1.289e+005	1.289e+005
Liq Vol Flow (m3/h)	70.02	124.8	194.9	194.9	223.3
v (kJ/h)	-9.814e+007	-5.651e+005	-9.871e+007	-4.964e+007	-4.964e+007
thalpy (kJ/kgmole)	-7.510e+004	-151.0	-1.955e+004	-9830	-7244

	Liquid-A	COOL-in	COOL-out	Cooled Process Gas	H2O
raction	0.0000	0.0000	0.0000	1.0000	1.0000
ture (C)	800.3	19.85 *	62.85	243.1	293.0 *
(kPa)	100.0	100.0 *	100.0 *	100.0 *	100.0 *
w (kgmole/h)	0.0000	3.600e+004 *	3.600e+004	6852	2614 *
w (kg/h)	0.0000	6.485e+005	6.485e+005	1.289e+005	4.708e+004
Liq Vol Flow (m3/h)	0.0000	649.9	649.9	223.3	47.18
v (kJ/h)	0.0000	-1.029e+010	-1.017e+010	-1.701e+008	-6.057e+008
thalpy (kJ/kgmole)	-7244	-2.858e+005	-2.825e+005	-2.482e+004	-2.317e+005

	Steam	SHIFT-in	Products	Liquid-B	Q-100
raction	1.0000	1.0000	1.0000	0.0000	---
ture (C)	102.9 *	200.0 *	200.0 *	200.0	---
(kPa)	100.0 *	100.0	100.0	100.0	---
w (kgmole/h)	2614	9466	9466	0.0000	---
w (kg/h)	4.708e+004	1.760e+005	1.760e+005	0.0000	---
Liq Vol Flow (m3/h)	47.18	270.5	305.0	0.0000	---
v (kJ/h)	-6.232e+008	-7.933e+008	-8.420e+008	0.0000	4.907e+007
thalpy (kJ/kgmole)	-2.384e+005	-8.380e+004	-8.896e+004	-8.896e+004	---

	Q-101	Q-102			
raction	---	---			
ture (C)	---	---			
(kPa)	---	---			
w (kgmole/h)	---	---			
w (kg/h)	---	---			
Liq Vol Flow (m3/h)	---	---			
v (kJ/h)	-1.750e+007	-4.877e+007			
thalpy (kJ/kgmole)	---	---			

Unit Ops

ation Name	Operation Type	Feeds	Products	Ignored	Calc. Level
	Mixer	CH4 Air	Preheater Feed	No	500.0 *
	Mixer	Cooled Process Gas Steam	SHIFT-in	No	500.0 *
	Heater	Preheater Feed Q-100	POX-in	No	500.0 *
	Heater	H2O Q-101	Steam	No	500.0 *
	Gibbs Reactor	POX-in	Liquid-A POX-out	No	500.0 *
	Gibbs Reactor	SHIFT-in Q-102	Liquid-B Products Q-102	No	500.0 *
	Heat Exchanger	POX-out COOL-in	Cooled Process Gas COOL-out	No	500.0 *

* Specified by user.

Appendix A-3

- ATR Worksheet

Workbook: Case (Main)

Streams

	CH4	Air	H2O(1)	Steam-1	Heater Feed
action	1.0000	1.0000	0.0000	1.0000	0.9907
ure (C)	19.85 *	19.85 *	19.85 *	102.9 *	40.22
(kPa)	100.0 *	100.0 *	100.0 *	100.0	100.0
N (kgmole/h)	1277 *	3656 *	446.8 *	446.8	5380
v (kg/h)	2.048e+004	1.055e+005	8049	8049	1.340e+005
Liq Vol Flow (m3/h)	68.40	121.9	8.066	8.066	198.4
' (kJ/h)	-9.587e+007	-5.796e+005	-1.277e+008	-1.065e+008	-2.030e+008
halpy (kJ/kgmole)	-7.510e+004	-158.5	-2.858e+005	-2.384e+005	-3.773e+004

	ATR-in	ATR-out	Liquid-A	COOL-in	COOL-out
action	1.0000	1.0000	0.0000	0.0000	0.7165
ure (C)	340.0 *	799.0	799.0	19.85 *	99.59
(kPa)	100.0	100.0	100.0	100.0 *	100.0
N (kgmole/h)	5380	7157	0.0000	3600 *	3600
v (kg/h)	1.340e+005	1.340e+005	0.0000	6.485e+004	6.485e+004
Liq Vol Flow (m3/h)	198.4	230.3	0.0000	64.99	64.99
' (kJ/h)	-1.460e+008	-1.460e+008	0.0000	-1.029e+009	-9.006e+008
halpy (kJ/kgmole)	-2.715e+004	-2.040e+004	-2.040e+004	-2.858e+005	-2.502e+005

	Process Gas	H2O(2)	Steam-2	SHIFT-in	Products
action	1.0000	0.0000	1.0000 *	1.0000	1.0000
ure (C)	240.9	19.85 *	99.59	199.9 *	199.9 *
(kPa)	100.0	100.0 *	100.0	100.0	100.0
N (kgmole/h)	7157	2553 *	2553	9710	9710
v (kg/h)	1.340e+005	4.599e+004	4.599e+004	1.800e+005	1.800e+005
Liq Vol Flow (m3/h)	230.3	46.09	46.09	276.4	306.7
' (kJ/h)	-2.743e+008	-7.297e+008	-6.090e+008	-8.833e+008	-9.262e+008
halpy (kJ/kgmole)	-3.832e+004	-2.858e+005	-2.385e+005	-9.096e+004	-9.538e+004

	Liquid-B	Q-100	Q-101	Q-102	Q-103
action	0.0000	---	---	---	---
ure (C)	199.9	---	---	---	---
(kPa)	100.0	---	---	---	---
N (kgmole/h)	0.0000	---	---	---	---
v (kg/h)	0.0000	---	---	---	---
Liq Vol Flow (m3/h)	0.0000	---	---	---	---
' (kJ/h)	0.0000	2.117e+007	5.695e+007	1.207e+008	4.284e+007
halpy (kJ/kgmole)	-9.538e+004	---	---	---	---

Unit Ops

ation Name	Operation Type	Feeds	Products	Ignored	Calc. Level
	Heater	H2O(1) Q-100	Steam-1	No	500.0 *
	Heater	Heater Feed Q-101	ATR-in	No	500.0 *
	Heater	H2O(2) Q-102	Steam-2	No	500.0 *
	Mixer	CH4 Air Steam-1	Heater Feed	No	500.0 *
	Mixer	Process Gas Steam-2	SHIFT-in	No	500.0 *
tor	Gibbs Reactor	ATR-in	Liquid-A ATR-out	No	500.0 *
	Gibbs Reactor	SHIFT-in Q-103	Liquid-B Products	No	500.0 *

* Specified by user.

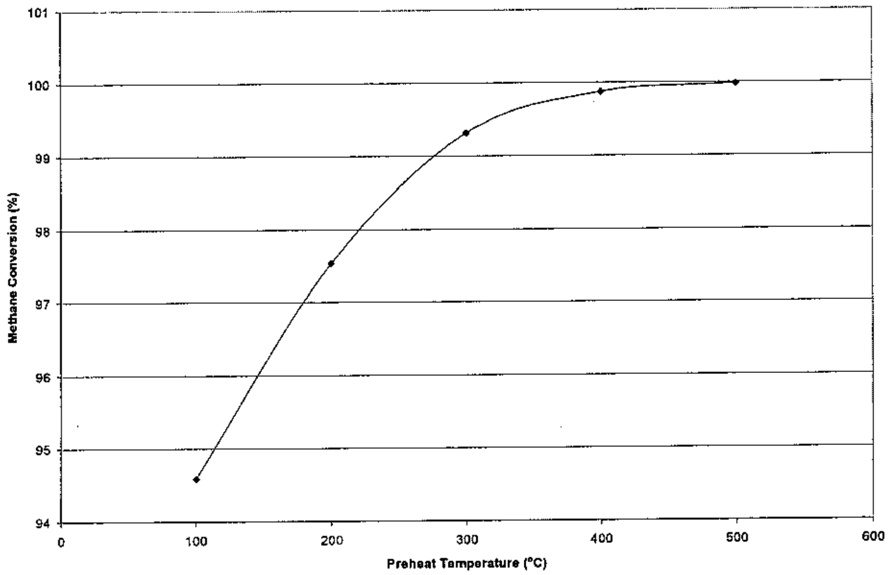
Workbook: Case (Main) (continued)

Unit Ops (continued)

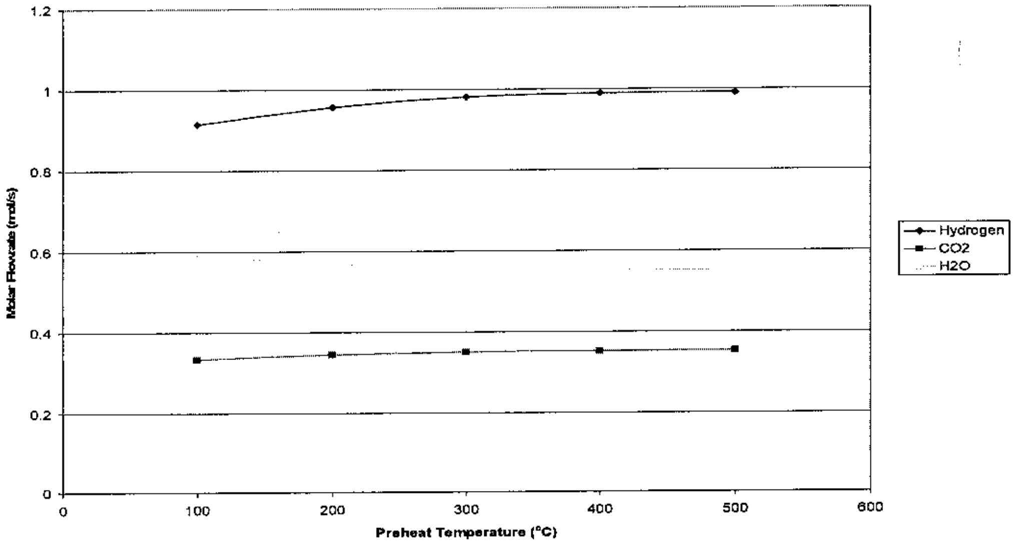
ation Name	Operation Type	Feeds	Products	Ignored	Calc. Level
	Gibbs Reactor		Q-103	No	500.0 *
	Heat Exchanger	ATR-out COOL-in	Process Gas COOL-out	No	500.0 *

* Specified by user.

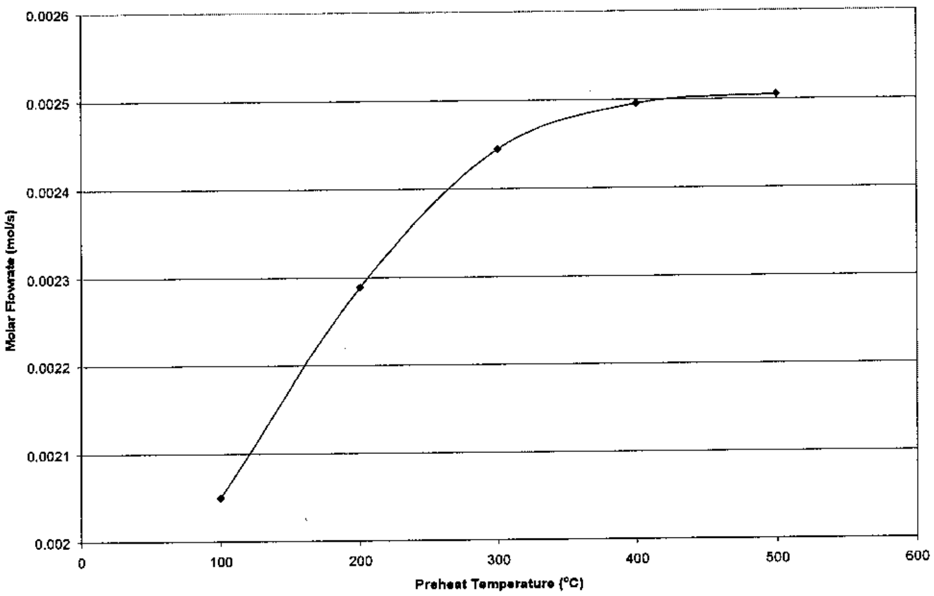
Appendix B-1



Graph methane conversion (%) against preheat temperature (°C) for auto thermal reforming (ATR) at equilibrium compositions



Graph product (H_2, CO_2, H_2O) molar flow rate (mol/s) against preheat temperature (°C) for auto thermal reforming (ATR) at equilibrium compositions



Graph product (CO) molar flow rate (mol/s) against preheat temperature (°C) for auto thermal reforming (ATR) at equilibrium compositions

Appendix C-1

SMR simulation results

thane l l/hr)	Methane Uncoverted(mol/hr)	Methane Conversion(%)	H2 (mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
909.360	459.050	49.519	1798.900	2.332	447.980	1375.100
909.360	372.460	59.042	2144.100	3.516	533.380	1294.100
909.360	289.250	68.192	2475.500	4.965	615.150	1220.000
909.360	212.100	76.676	2782.500	6.599	690.670	1158.300
909.360	145.690	83.979	3046.500	8.187	755.480	1118.000
909.360	95.585	89.489	3245.700	9.355	804.420	1109.900
909.360	63.093	93.062	3375.200	9.879	836.390	1136.400
909.360	43.627	95.202	3453.000	9.890	855.840	1188.400
909.360	31.811	96.502	3500.600	9.625	867.920	1255.400
909.360	24.247	97.334	3531.200	9.243	875.870	1330.800
909.360	19.120	97.897	3552.100	8.825	881.410	1411.100
909.360	15.489	98.297	3567.100	8.407	885.460	1494.400
909.360	12.804	98.592	3578.200	8.007	888.550	1579.500
909.360	10.759	98.817	3586.800	7.631	890.470	1666.000
909.360	9.163	98.992	3593.500	7.281	892.920	1753.200
909.360	7.887	99.133	3598.900	6.955	894.520	1841.400
909.360	6.854	99.246	3603.400	6.655	895.850	1930.000
909.360	6.003	99.340	3607.100	6.376	896.980	2019.000
909.360	5.294	99.418	3610.100	6.118	897.950	2108.200
909.360	4.697	99.483	3612.800	5.879	898.780	2197.700
909.360	4.190	99.539	3615.000	5.657	899.510	2287.400
909.360	3.755	99.587	3617.000	5.450	900.150	2377.300
909.360	3.380	99.628	3618.700	5.257	900.720	2467.300
909.360	3.054	99.664	3620.100	5.077	901.230	2557.400
909.360	2.769	99.695	3621.500	4.909	901.680	2647.600
909.360	2.519	99.723	3622.600	4.751	902.090	2737.900

ethane ed nol/hr)	Methane Uncoverted(mol/hr)	Methane Conversion(%)	H2 (mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
909.36	765.990	15.766	573.370	0.100	143.270	3259.700
909.36	599.160	34.112	1240.300	0.523	309.680	2926.500
909.36	337.790	62.854	2284.100	2.153	569.420	2405.400
909.36	82.979	90.875	3299.900	5.674	820.710	1899.300
909.36	9.163	98.992	3593.500	7.281	892.920	1753.200
909.36	1.088	99.880	3625.600	7.479	900.790	1737.300
909.36	0.172	99.981	3629.300	7.501	901.690	1735.500

Appendix C-2

POX simulation results

	Methane fed(mol/hr)	Methane Unconverted(mol/hr)	Methane Conversion	H2(mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
.0	1306.8	1306.8000	0.000	0.00	0.00	0.00	2613.60
.1	1306.8	875.1800	33.029	1202.80	0.91	430.71	2274.10
.2	1306.8	403.2600	69.141	2563.60	4.93	898.61	1857.00
.3	1306.8	13.4630	98.970	3593.80	11.40	1281.90	1606.50
.4	1306.8	0.0016	100.000	3128.30	7.70	1299.10	2098.90
.5	1306.8	0.0000	100.000	2608.00	5.16	1301.60	2619.20

at	Methane Fed (mol/hr)	Methane Uncoverted(mol/hr)	Methane Conversion(%)	H2 (mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
0	1306.8	81.281	93.780	3324.7	9.2428	1216.3	1740
0	1306.8	43.214	96.693	3475.8	10.404	1253.2	1665
0	1306.8	15.542	98.811	3585.6	11.332	1279.9	1610.6
0	1306.8	3.5183	99.731	3633.2	11.759	1291.5	1586.9
0	1306.8	0.685	99.948	3644.4	11.861	1294.3	1581.4

	Methane Fed (mol/hr)	Methane Uncoverted(mol/hr)	Methane Conversion(%)	H2 (mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
	1306.8	816.36	37.530	393.39	0.23983	490.2	3201.1
	1306.8	659.96	49.498	1018.3	0.90619	645.93	2889
	1306.8	373.2	71.442	2162.8	3.4528	930.15	2318
	1306.8	104.11	92.033	3234	8.6043	1194.1	1785
	1306.8	13.563	98.962	3593.4	11.401	1281.8	1606.7
	1306.8	1.59	99.878	3640.9	11.828	1293.4	1583.2
	1306.8	0.24283	99.981	3646.2	11.877	1294.7	1580.5

Appendix C-3

ATR simulation results

ethane ed(mol/hr)	Methane Unconverted(mol/hr)	Methane Conversion(%)	H2(mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
1276.6	1238.9	2.953	150.51	7.87E-03	37.621	2860.7
1276.6	775.74	39.234	1491.5	1.21	499.61	2446.1
1276.6	304.3	76.163	2862.5	5.4437	966.82	2018
1276.6	1.2863	99.899	3560.1	9.2853	1266	1926.4
1276.6	5.28E-04	100.000	3057.6	6.3404	1270.2	2431.5
1276.6	6.17E-06	100.000	2549	4.3787	1272.2	2940.1

ethane ed(mol/hr)	Methane Unconverted(mol/hr)	Methane Conversion(%)	H2(mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
1276.6	1227	3.885	198.09	1.21E-02	49.513	3219.9
1276.6	751.13	41.162	1589.9	1.1911	524.24	2779.9
1276.6	280.57	78.022	2957.9	4.9458	991.05	2353.1
1276.6	0.98252	99.923	3562.8	7.7708	1267.8	2307.3
1276.6	5.94E-04	100.000	3058.5	5.4852	1271.1	2813.6
1276.6	7.51E-06	100.000	2549.5	3.8774	1272.7	3322.6

ethane ed(mol/hr)	Methane Unconverted(mol/hr)	Methane Conversion(%)	H2(mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
1276.6	1216.9	4.676	238.52	1.58E-02	59.618	3582.7
1276.6	733.41	42.550	1660.9	1.1436	542	3127.4
1276.6	263.06	79.394	3028.3	4.4925	1009	2700.6
1276.6	0.86073	99.933	3564.4	6.6781	1269	2688.9
1276.6	6.91E-04	100.000	3059.1	4.8331	1271.7	3196
1276.6	9.21E-06	100.000	2549.9	3.479	1273.1	3705.2

ethane ed(mol/hr)	Methane Unconverted(mol/hr)	Methane Conversion(%)	H2(mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
1276.6	1207.5	5.413	276.17	1.92E-02	69.028	3946.8
1276.6	719.65	43.628	1716	1.0881	555.83	3482.8
1276.6	249.16	80.483	3084.4	4.1021	1023.3	3055.4
1276.6	0.80547	99.937	3565.4	5.8538	1269.9	3071
1276.6	8.13E-04	100.000	3059.6	4.3195	1272.2	3578.4
1276.6	1.13E-05	100.000	2550.2	3.1549	1273.4	4087.8

Appendix C-3

ATR simulation results(cont.)

Methane Fed (mol/hr)	Methane Uncoverted(mol/hr)	Methane Conversion(%)	H2 (mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
1276.6	69.17	94.582	3290.5	7.3784	1200	2124.1
1276.6	31.424	97.538	3440.6	8.2414	1236.9	2049.5
1276.6	8.7808	99.312	3530.6	8.7998	1259	2004.8
1276.6	1.6755	99.869	3558.8	8.9818	1265.9	1990.7
1276.6	0.31235	99.976	3564.2	9.0171	1267.2	1988.1

ethane ed nol/hr)	Methane Uncoverted(mol/hr)	Methane Conversion(%)	H2 (mol/hr)	CO(mol/hr)	CO2(mol/hr)	H2O(mol/hr)
1276.6	769.87	39.694	494.74	0.28291	506.41	3518.4
1276.6	588.32	53.915	1220.2	1.0552	687.19	3156.1
1276.6	286.48	77.559	2424.9	3.7165	986.36	2555.1
1276.6	50.432	96.050	3365	7.7966	1218.3	2087.1
1276.6	4.523	99.646	3547.5	8.9085	1263.1	1996.4
1276.6	0.50263	99.961	3563.5	9.0121	1267	1988.4
1276.6	0.076723	99.994	3565.2	9.0232	1267.5	1987.6