Simulation of Methane Slippage in Steam Methane Reforming

by

Mohd Fahmi Bin Zulkefli

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

SEPTEMBER 2011

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr. Lemma Dendena Tufa)
Final Year Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
September 2011

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.

MOHD FAHMI BIN ZULKEFLI

ABSTRACT

Hydrogen production technologies have emerged as a one of the most researched and promising future global energy. Hydrogen economy is a vision for future in with hydrogen replaced conventional power sources to reduce addiction on non-renewable energy and to drastically reduced harmful emissions to the environment. For this technology, hydrogen is mostly produced from hydrocarbons. Therefore, many research have been conducted on hydrogen production from hydrocarbons to find the most economical, efficient and practical method of producing hydrogen. On this research, a simulation plant model using steam methane reforming has been designed to observe methane slippage effect at reformer. From the simulation plant model, an analysis on the causes and effects of the methane slippage process is determined based on variation of composition in feedstock (natural gas). Based on several cases that contribute to high methane slippage namely variation of carbon dioxide content in natural gas, steam to carbon ratio and reformer outlet temperature are highlighted in the report.

This research was carried out using computational tools, which is Aspen HYSYS 2006. Aspen HYSYS 2006 provides tool to design a steady and dynamics state simulation plant model of hydrogen production from methane. The software also allows us to study and analyze the process directly, by manipulating the process variable and unit operation topology. There are two steps to be follow in order to develop and analyze the simulation plant model, begin with base case development and base case validation. Validation of this simulation data has been compared with actual data from Petronas Fertilizer Kedah (PFKSB), an ammonia plant in Malaysia.

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The internal examiners I owe a debt of thanks, as they lead us onto a better path towards improving the project, as well as my minds, and way of thinking. Their comments have been reflected in my report as I strive to fix the mistakes I may have made during my presentation. Thank you also to all lecturers and staff that were (are) directly and indirectly involved in making this project a success.

Of course, perhaps most importantly, I thank my loved ones for their emotional and otherwise support, and I am grateful to have them in our lives.

Sincerely,
Mohd Fahmi Bin Zulkefli

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF EQUATIONS

CHAPTER 1

INTRODUCTION

1.1 Background of study

The use of hydrogen for petrochemicals, fertilizers and as energy carrier in connection with renewable energy production will increase substantially in the next 5-10 years as even more stringent environmental legislation is enforced. Hydrogen will be required by refiners and specialty chemical manufacturers to meet the global need for cleaner products. The growing fuel cell market will be dependent on hydrogen as a primary fuel source.As the world moving forward, these energy carriers are produced by the conversion of fossil sources, mainly hydrocarbons and nuclear energy, into an energy form that is in a usable form to industrial, commercial, residential, and transportation end-users. The sustainable energy supply system of the future would features in form of electricity and hydrogen as the most in demand energy carriers. Importantly, hydrogen would be produced from a very diverse base of primary energy feedstock using the resources and processes that are most economical or consciously preferred. Although natural gas will likely provide the earliest affordable feedstock for hydrogen, today's costs are prohibitively expensive. The cost of producing and delivering hydrogen from a small scale reformer of natural gas for a fuel cell vehicle could be as high as $40 per million BTUs with today's technology (Fereidun Fesharaki, June 2000).

Steam methane is the catalytic gas phase conversion of energy carriers, in this case is natural gas described as hydrocarbon, using steam into a mixture of carbon monoxide, carbon dioxide and hydrogen. The product mixture of the reactions is known as reformate. The reaction is endothermic and thus requires a heat supply. Besides hydrogen, and carbon monoxide, reformate usually contains significant amounts of unconverted steam and to a lesser extent some unconverted methane and carbon dioxide which later being formed by the consecutive water gas shift reaction.

Currently, almost all hydrogen is produced via steam reforming of natural gas, over 95% of all hydrogen produced in the U.S. and 48% globally (Fereidun Fesharaki, June 2000). The demand for hydrogen is growing in many industries, particularly in the chemical and refining industries. Steam reforming of hydrocarbons for industrial application such as ammonia production was introduced in 1930 (Agarwal, 2011). Hydrogen also being utilizes in conversion of heavy petroleum fractions into lighter ones via hydro cracking and other petroleum fractions. Since then, the technology has experienced revolutionary changes in its energy consumption patterns. National Renewable Energy Laboratory (NREL) assessment on hydrogen production via steam reforming reported that most of the energy consumed, about 87.1%, is that contained in the natural gas fed to the steam reformer. Table 1.1 shows the average energy requirements (LHV basis) of steam reforming that was reported in the report.

	System total energy consumption (MJ/kg H2)	**% of total in this table**	**% of total from construction & decommissioning**	**% of total from natural gas production**	**% of total form electricity generation**	**% of total from avoided opeartions**
Energy in the natural gas to hydrogen plant	159.6	87.1	N/A	100.0	N/A	N/A
Non feedstock energy consumed by system	23.6	12.9	2.4	169.8	17.0	-89.3
Total energy consumed by system	183.2	N/A	N/A	N/A	N/A	N/A

Table 1.1: Average energy requirements (LHV basis) from *(Mann, Febuary 2001)*

The majority of the total energy consumption comes from natural gas production and distribution (see Table 1.1), which can be further broken up into sub-processes: natural gas extraction, processing, transmission, storage, and distribution. Analyzing each of these steps, it was found that the large amount of energy consumed in natural gas production is specifically from the natural gas extraction and transport steps. The energy in the natural gas is greater than the energy content of the hydrogen produced; more energy is consumed by the system than is produced. In order to obtain acceptable reaction rates, condition of catalytic tubes in the reformer must be in optimum condition and reaction heating value is sufficient to ensure acceleration of the reaction.

Hydrogen production processes are in various stages of development. Some technologies, mainly steam methane reforming, are becoming well-developed and can be used in the near term. Development of steam reforming is being done intensively over the past decade due to high demand of hydrogen. In general, research is focused on reducing capital equipment, operations, and maintenance costs, as well as improving the efficiency of steam methane reforming. Several research groups are actively involved in the development of new catalysts and reactor designs for steam methane reforming to hydrogen makeup gas in a more energy-efficient manner (Lui, 2006; Tsang et al., 1995; Pen˜a et al., 1996).

1.2. Problem Statement

This research is study on methane slippage in hydrogen production from steam methane reforming. Methane slippage is the amount of methane that escapes from a column (reformer) along with products, where it is undesirable. In conventional steam methane reforming (SMR), it is desirable to minimize the amount of unconverted hydrocarbons leaving the reformers. In industry application, methane that passes through the reformer will eventually recycle back into reformer for start up operation and it is not favourable that methane being released to atmosphere. Recycle loop is not the favourable solution either as it will accumulate in the system before it reaches process throughput. If build up were left inside the loop, the partial pressure of the other components would be reduced to the point where the reaction rate would be uneconomically slow (Osman, 1984) could impact on production effectiveness of the plant. Therefore, it is important to find a proper, economical and simple solution on minimizing amount of methane slippage.

Hydrogen production via steam methane reforming with validated data taken from an ammonia plant application. It is important to study the design parameter for methane steam reformer before design the process model in simulation environment. So to conduct this study, the optimized model of hydrogen production used methane as raw material has been developed using Aspen HYSYS 2006 software and equipment data specification from an industrial application.

1.3. Objective of Study

Main objective: To simulate methane slippage in steam methane reforming process.

Sub-objectives:

To achieve main objective these sub-objectives are to be highlighted:

1. To investigate the effects of carbon dioxide composition in natural gas (feedstock), steam to carbon ratio (S/C) and reformer outlet temperature on methane slippage.
2. To design steady state model of steam methane reforming process by using Aspen HYSYS software.
3. To validate and compare simulation with industry application/journal data.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrogen production

Hydrogen for use in ammonia plant is produced by the catalytic reforming of hydrocarbons. Diesel, jet fuel, gasoline, as well as natural gas, are potential fuels that all have existing infrastructure of manufacture and distribution, for hydrogen production. Most of the ammonia plant used natural gas as source of hydrogen due to its price and it is a proved and matured process technology in compared with others. Among hydrocarbons, natural gas especially methane is also the most common and traditional source for producing hydrogen for fuel cell application (Hoang et al., 2005).

2.2 Hydrogen production from steam methane reforming

Production of hydrogen comes primarily from two sources, catalytic reforming of natural gas from the dehydrogenation of naphtha into aromatics and high-octane gasoline blend stocks, as well as from direct hydrogen manufacture. The bulk of direct hydrogen manufacturing in a petroleum refinery is still accomplished via either steam-methane reforming (Figure 2.1) or steam methane reforming.

In the overall steam methane reforming (SMR) reaction, methane reacts with steam at high temperatures and moderate pressures in catalyst-filled tubes to generate synthesis gas, a mixture of hydrogen, carbon monoxide and some carbon dioxide. The reactions for the two simultaneous SMR mechanisms are shown as Equations (Equation 2.1) and (Equation 2.2). Both are endothermic, as shown by the positive heat of reaction. The reactions require heat transfer to maintain temperatures favorable to the equilibrium reactions.

$CH_4+H_2O \leftrightarrow CO+3H_2$ (steam reforming, $\Delta H = 206.3$ kJ/mol)

(Equation 2.1)

$CH_4+2H_2O \leftrightarrow CO_2+4H_2$ (methanation, $\Delta H = 165$ kJ/mol)

(Equation 2.2)

Additional hydrogen can be generated from the carbon monoxide by product following the reforming reaction. Note the water-shift reaction (Equation 2.3) is exothermic, which results in a temperature increase across the reactors as water reacts with CO to form CO_2 and more H_2.

$CO+H_2O \leftrightarrow CO_2+H_2$ (water gas shift, $\Delta H = -41.2$ kJ/mol)

(Equation 2.3)

Water shift gas equilibrium is not affected by pressure, since there is no volume change. Essentially, the oxygen atom is stripped from the additional steam to oxidize CO to CO_2. This oxidation also provides energy to maintain the reaction. Additional heat required to drive the process is generally supplied by burning some portion of the methane. Reduced temperatures favour the conversion of CO to H_2, as might be expected by its exothermic nature.

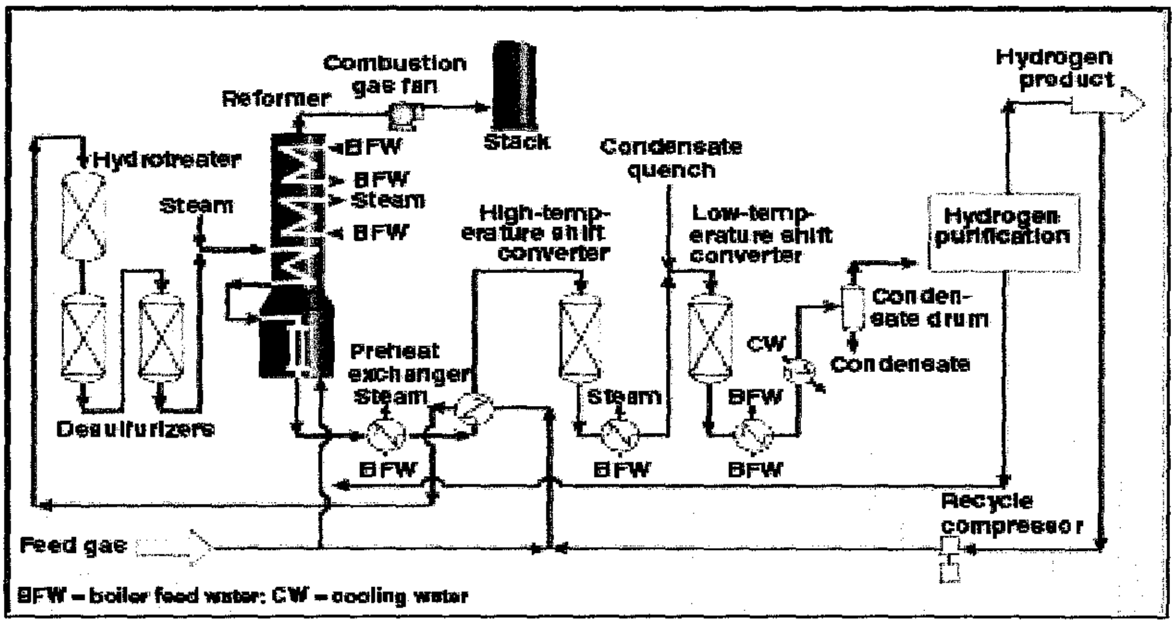


Figure 2.1: Steam-methane reforming is still responsible for the bulk of hydrogen production in petroleum refineries. *(Sources: Synetix)*

In general, reforming reactions are catalyzed by group 8-10 metals with nickel as the preferred metal for industrial application because of its activity ready availability and low cost (Lui, 2006). Methane is activated on the nickel surface. The resulting CH_x species then reacts with OH species adsorbed on the nickel or on the support (Rostrup-Nielsen, J.R., 2001).

2.2.1 Hydrocarbon feedstock

Below, describes about the researches that have been done for methane as input for hydrogen production.

Yi-Ning and Rodrigues (2005) described an experiment on hydrogen production from steam methane reforming (SMR) coupled with in situ CO_2 capture. In this work, instead of using complex model, a simplified two-section reactor model is proposed for analyzing the SMR adsorptive reactor system. The first section contains the catalyst only. The second section contains a mixture of the catalyst and the CO_2 selective chemisorbent. One of the objectives in this study is to understand the process implication within the complicated SE-SMR reactor. Ochoa-Ferna′ndez et al. (2005) discussed the sorption enhanced hydrogen production by steam methane reforming using Li_2ZrO_3 as sorbent. The results show that the process is capable of directly producing concentrations of H_2 larger than 95 mol% with methane as the main side product with less than 0.2 mol% of CO. Tong and Matsumura (2005) discussed the pure hydrogen production by methane steam reforming with hydrogen-permeable membrane reactor. The methane conversion with the reactor is significantly higher than its equilibrium value without membrane due to the equilibrium-shift combined with separation of pure hydrogen through the membrane.

Steam methane reforming is commonly used natural gas as feedstock, and later then being converted into hydrogen in refineries. Natural gas is not a commodity with uniform composition, and the precise composition can have important implications for simulation model and also optimal operating condition of a plant. The simple assumption that natural gas is consists only pure methane is acceptable in process modelling and would not lead to an irrelevancy of the model. Table 2.1 states range of natural gas composition and the baseline composition chosen for the simulation model.

Table 2.1: Natural gas composition (*Mann, Febuary 2001*)

Component	**Normal range (a)**	**Typical range of components (mol%) (b)**	
	Mol % (dry)	**Low value**	**High value**
Methane, CH_4	94.5	75	99
Ethane, C_2H_6	2.7	1	15
Propane, C_3H_8	1.5	1	10
Carbon dioxide, CO_2	0.5	0	10
Nitrogen, N_2	0.8	0	15
Hydrogen sulfide, H_2S	0	0	30
Heat of combustion, HHV	53.689 kJ/g	-	-

(a) Taken from SRI, 1994.

(b) Taken from Ullmann's Encyclopedia of Industrial Chemistry, 1986.

Fluctuations of carbon dioxide content in natural gas will be main issue as quality of natural gas is different. Even so, the project will concentrate on ASEAN region as its development and demand for natural gas are more stable than in other regions in the world (Fereidun Fesharaki, June 2000).

2.2.2 Operating conditions

Natural gas feed is preheated in coils in the waste heat section of the reformer, and sulfur is removed over a zinc oxide catalyst. Process steam is added, and the mixture of natural gas and steam is further preheated before entering the tubular reformer. Here, conversion to equilibrium of hydrocarbons to hydrogen, carbon monoxide and carbon dioxide takes place over a nickel based reforming catalyst.

Steam reformer converts a hydrocarbon feed (natural gas) to hydrogen and carbon monoxide by means of endothermic reaction with steam. In provide a mixture of H_2, CO, H_2O, small fractions of CO_2 and non-reacted CH_4. The produced H_2/CO ratios depend on the feedstock, CO2 recycle and operating condition such as temperature and pressure outlet of the reformer. The primary reformer operating condition for outlet temperature range is 750-850°C and outlet pressure is about 40 - 42 bar (Rostrup-Nielsen, J.R, 2002). Then followed by treatment of partially reformed gas in secondary reformer to which process air is introduced. At these conditions, all heavier hydrocarbons are completely converted to hydrogen, carbon monoxides and carbon oxides. Only methane, carbon monoxide, carbon dioxide, hydrogen and steam exist at the outlet of the steam reformer. Based on Figure 2.2, a reformed gas is produced in reformer having a greater amount of hydrogen and a lesser amount of hydrocarbons.

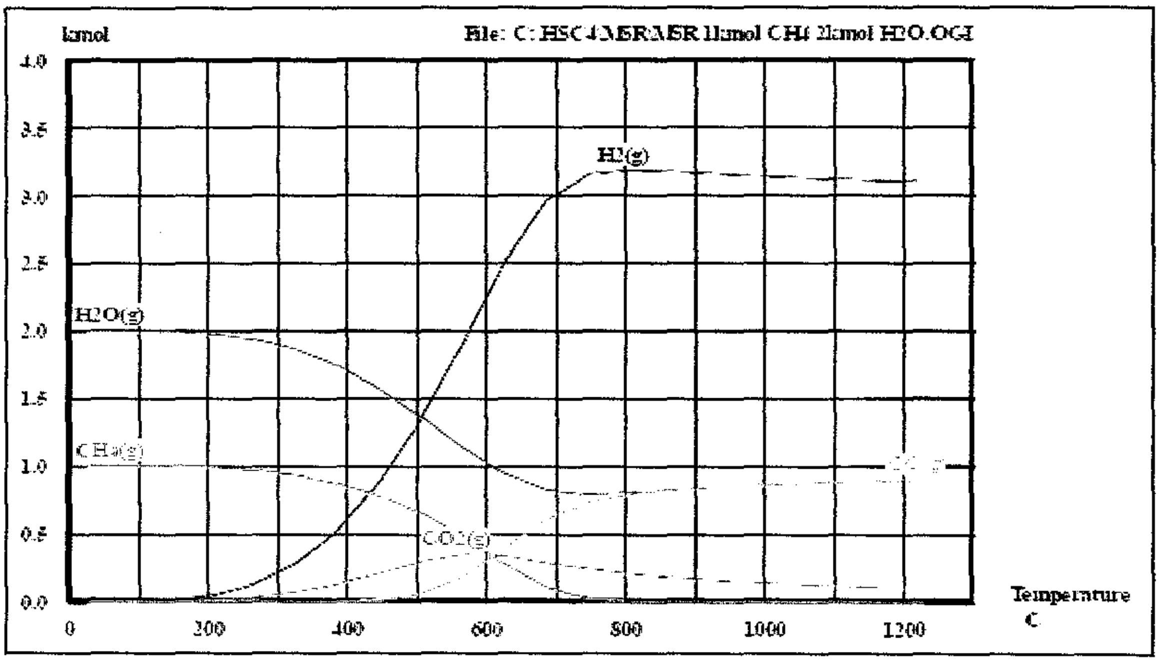


Figure 2.2: Theoretical thermodynamics for steam methane reforming process *(James A. Liu, 2006)*

Product gas from the steam reforming contains equilibrium amounts of hydrogen, carbon dioxide, carbon monoxide and excess steam. Excess steam above the theoretical requirements is maintained to prevent the reforming catalyst from coking. The temperature exiting the reformer furnace tubes is usually about 760°C, a level that provides maximum hydrogen production within the temperature limitation of the reformer tube metallurgy (Rostrup-Nielsen, J.R., 2002).

2.3 Reformer modelling.

Simulation can assist researchers to better design, optimize, control and operate our chemical process plant. Feed and environmental disturbances, heat exchanger fouling, and catalytic degradation continuously upset the conditions of a smooth running process. The transient behaviour of the process system is best studied using a dynamic simulation tool like HYSYS and any other simulation tools. The design and optimization of a chemical process involves the study of both steady state and dynamic behaviour. Steady state models can perform steady state energy and material balances and evaluate different plant scenarios. The design can be use steady state simulation to optimize the process by reducing capital and equipment costs while maximizing production. With dynamic simulation, we can confirm that the plant can produce the desired product in a manner that is safe and easy to operate. By defining detailed equipment specifications in the dynamic simulation, you can verify that the equipment will function as expected in an actual plant situation.

Steady and dynamics state reforming model for the steam methane reforming process have been developed various times. The steady state model is based on a model described by Svendsen et al. (1996).The model is implemented in gPROMS (1997) (general Process Modeling System) which is a combined discrete/continuous modeling environment for chemical processing systems. The main reactions taking place are the endothermic reactions which have been stated previously.

2.4 Methane slippage.

In recent years, development to maximize conversion of hydrocarbon concentrates on manipulating the purge recovery units such as cryogenic fractionation and pressure swing adsorption (Osman, 1984). Unfortunately, methane slippage occurs mainly at reforming unit where hydrocarbon first enters the process plant. Purge recovery unit, mostly situated at the back end of a plant. Manipulating the purge recovery unit doesn't solve the problem and it would only transfer the problem to other process units.

Patent by W.H. Marshall (1963) stated that by employs steam to carbon ratio of 4 to 8 hydrocarbon conversion of 65% to 85% of hydrogen and carbon dioxide, could be achieved respectively. The patent elaborates more that conversion is increased further to 95% - 98% in reformer which will minimize the methane slippage in the reformer loop. This solution however doesn't seem economically feasible for current industrial situation because it would increase energy consumption of the process.

In steam methane reformer, reactants were indirectly heated with much assistant by catalysts. Without catalyst, it is impossible to archive such high temperature. Studies of suitable catalyst in steam reformer have been somewhat new perspective in maximizing conversion of hydrocarbon. James Liu (2006) studied kinetics of various suitable catalysts that can be use in steam reforming. Theoretically, ceramic-supported nickel catalyst in reformer can archive high conversion of hydrocarbon, but the supported catalyst would suffer from deactivation by particle sintering or by reaction with supports, thermal deterioration of the support and carbon deposition (Lui, 2006). The studies also briefly explain on other suitable catalysts such as rhodium, ruthenium, palladium and platinum. In the case of solving the problem, the thesis proved that catalysts can be a factor on maximizing conversion in steam reformer.

Relationship between increase methane slippage at reformer outlet with fluctuation of carbon dioxide content in natural gas is illustrated in Figure 2.3.

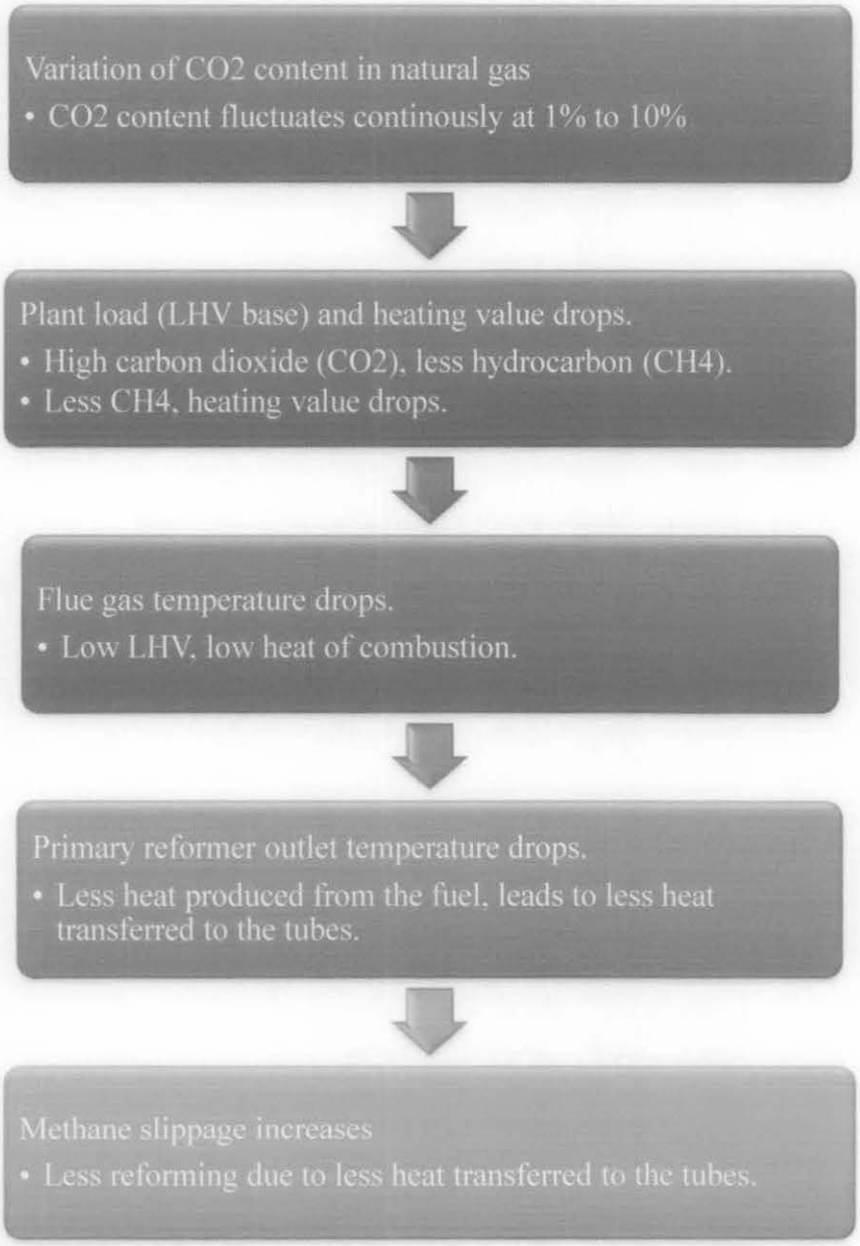


Figure 2.3: Hypothesis impact of methane slippage due to variation of CO2 content in natural gas in steam methane reforming. (Petronas Fertilizer Kedah, *PFKSB, 2010*)

2.4.1 Effects of methane slippage

The equilibrium calculation from the reforming model was performed to figure out the required steam-to-carbon ratio (S/C = 0–5) and reforming temperature (250–1200°C) where coke formation was thermodynamically unfavorable. S/C, reforming temperature and product species strongly contributed to the coke formation and product composition.

Formation of coke during the catalytic steam reforming could lead to deactivation of catalysts, resulting in low durability, reforming reaction activity and waste of valuable feedstock. Thus it is important to keep it under control because it could effects the reformer operation and environment in long run. Operating the reforming system under the coke-free region could avoid the coke formation. Based on a study made by Kajornsak Faungnawakij et.al (2006) on thermodynamic analysis of carbon formation in steam methane reforming of dimethyl ether (DME), shown that there are significant different between cases where feedstock component are being manipulated to see effect on coke formation. Figure 2.4 illustrates the findings on coke free and non coke free region for both cases.

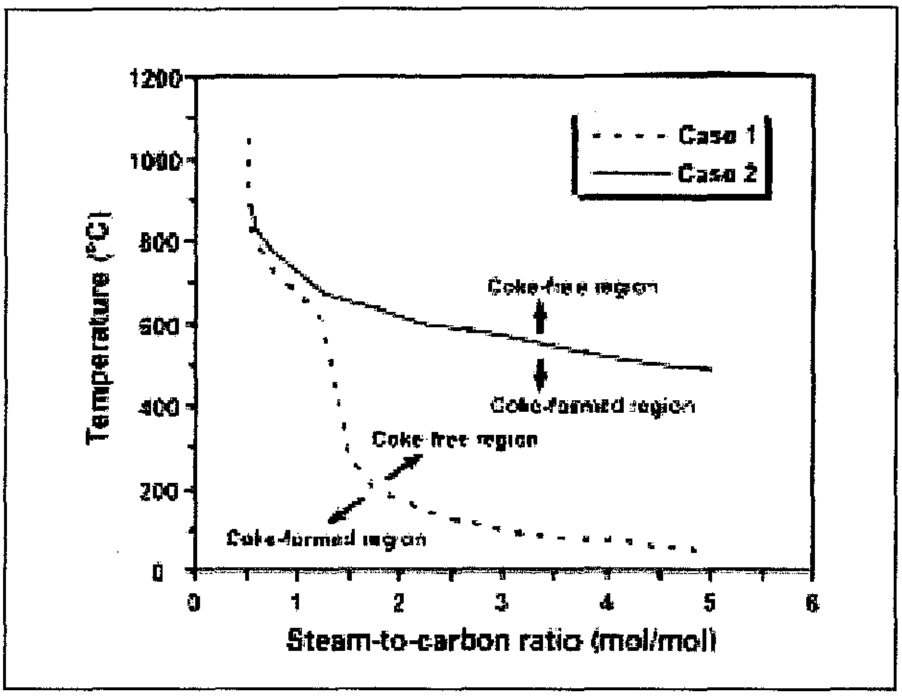


Figure 2.4: Coke formation boundary of DME as a function of steam-to-carbon (S/C) and temperature. (Kajornsak Faungnawakij et.al, 2006)

2.5 Summary

This chapter describes about the researches that have been done on hydrogen production from steam reforming process. Furthermore, there are many processes that produce hydrogen from hydrocarbon in this case steam reforming is described as preferred process. The main purpose of this literature review is to study about the hydrogen production; steam methane reforming and more importantly research on methane slippage in reformer. There are a few researchers had done their researches on hydrogen production from steam methane reforming and some of the researches are applied for this thesis.

CHAPTER 3

PROJECT METHODOLOGY

3.1 Research Tools

This research was carried out using computational tools. Aspen HYSYS 2006 was used to provide a simulation model of hydrogen production from methane. Flash and physical property calculations for this reaction can be provided by this Aspen HYSYS 2006 process simulator. This will allow us to define all information (property package, components, hypothetical components, interaction parameters, reaction, tabular data, etc) inside a single entity.

3.1.1 Aspen HYSYS 2006

aspentech

Aspen HYSYS

Aspen HYSYS 2006 is a core element of AspenTech's AspenONE® Engineering applications. Advantages for using HYSYS is we can create rigorous steady-state and dynamic models for plant design and trouble shooting. Through the completely interactive HYSYS interface, we have the ability to easily manipulate process variables and unit operation topology, as well as the ability to fully customize our simulation using its OLE extensibility capability.

3.2 Research Activities

3.2.1 Data collection

Data collection is the most important step in development of high fidelity models. The variation in the input/output data and the regions of operation are important factors in determining if the data is a good representation of process behaviour over a wide range of condition. At this stage, general understanding of the process has to be obtained whereby, both theoretical analysis and experience of the operators help identify the variables, variable relationships, approximately correlations and dynamic characteristic.

3.2.1 Base Case Development

HYSYS have produced an extremely powerful approach to steady and dynamic state modeling. At a fundamental level, the comprehensive selection of operation and property method can allow us to model a wide range of processes for the future. The base case of this study is being developed by finding and combining all the reactions that occurred in methane reactions with steam. All the reactions involved are written as below.

$CH_4 + H_2O \rightarrow CO + 3H_2$ (Equation 3.1)

$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$ (Equation 3.2)

All these two reactions are reacting in steam methane reformer in vapor phase. Total reaction for all the reactions are given as

$2CH_4 + 3H_2O \rightarrow CO_2 + CO + 7H_2$ (Equation 3.3)

Four different cases have been applied in which developed model is applied in order to determine the effect of variation of carbon dioxide towards methane slippage. Study on natural gas composition effect on methane slippage is based on four cases stated in Table 3.1.

Table 3.1: Composition of natural gas stream obtained from the HYSYS simulation.

Component	Case 1	Case 2	Case 3	Case 4
	Composition (mole fraction)			
Methane, CH_4	1.0000	0.9725	0.9000	0.8800
Carbon dioxide, CO_2	0.0000	0.0275	0.1000	0.1200

3.2.2 Base Case Validation

The process of hydrogen production from methane as a raw material was simulated using commercial flow sheeting software, Aspen HYSYS 2006. Validation was done by comparing the molar flow rate of the effluent by calculation from total reaction and the molar flow rate of the effluent of the process as simulated in Aspen HYSYS 2006 simulation and data from actual plant, Petronas Fertilizer Kedah an ammonia plant in Malaysia. Basis for calculation is 1000 kgmole/hr of methane feed.

3.3 Summary

This chapter describes the methodology used for this study. The methodology starts with stoichiometry mathematically analysis which produce the input and output calculations data. This data then used for base case development and validation. The result that obtained was discussed in Chapter 5. The project methodology was illustrated in Figure 3.1. The timeline of the project activities (Gantt chart) were illustrated in Appendix 1 and 2.

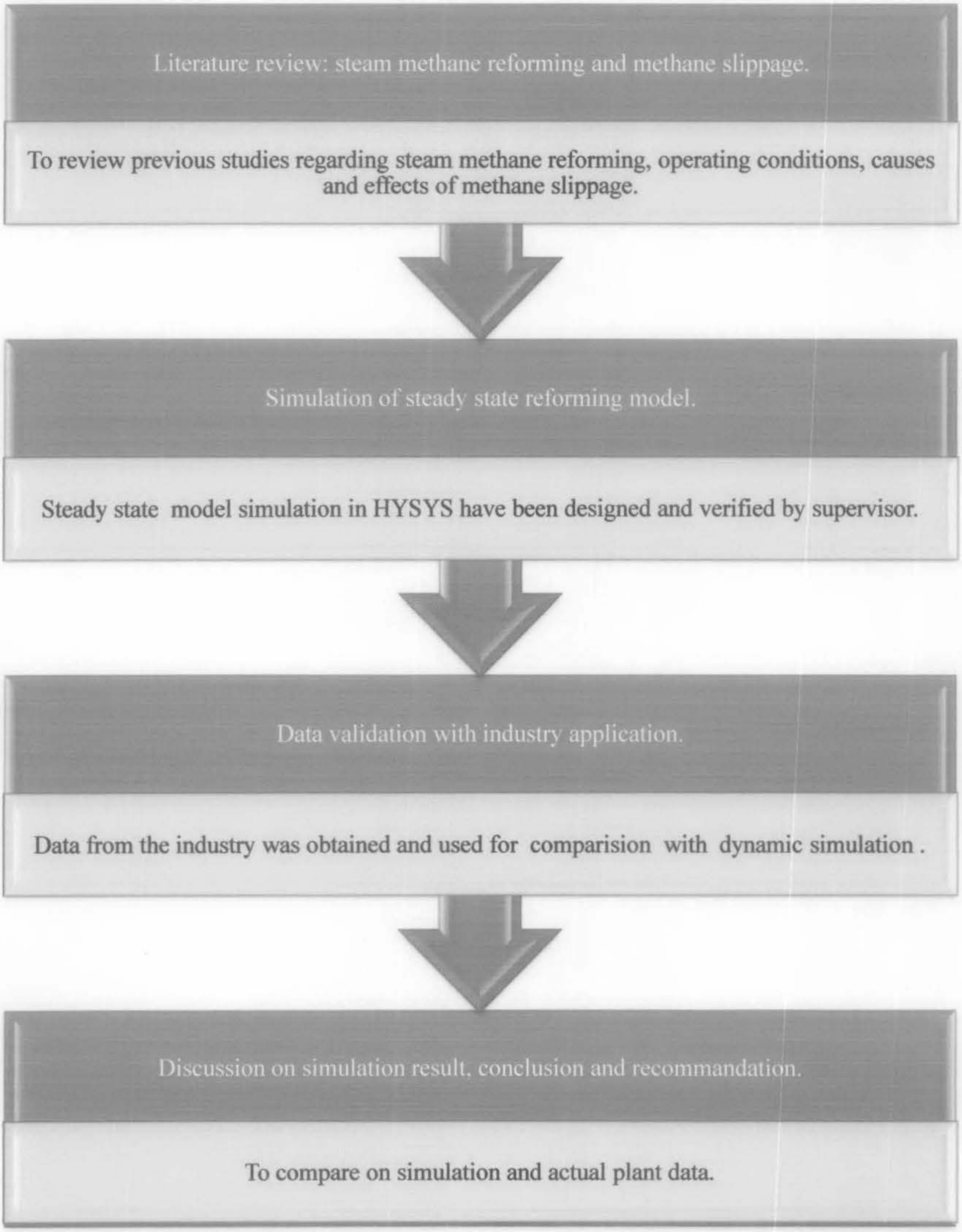


Figure 3.1: Project methodology of the project

CHAPTER 4

SIMULATION OF STEAM METHANE REFORMING

4.1 Modelling and Simulation of Hydrogen Production Process

The hydrogen production from ethane was simulated using Aspen HYSYS 2006. Typically the simulation process takes the following stages:

1. Preparation stage
    a. Selecting the thermodynamic model
    b. Defining chemical components
2. Building stage
    a. Adding and defining streams
    b. Adding and defining unit operations
    c. Connecting stream to unit operations
3. Execution stage
    a. Starting integration

Aspen HYSYS simulator is made up of four major parts to form a rigorous modeling and simulation environment.

1. A component library consisting of pure component physical properties
2. Thermodynamic packages for transport and physical properties prediction
3. Integrator for dynamic simulation and/or solver for stead-state simulation
4. Mathematical modeling of unit operation

4.1.1 Physical Properties of the Pure Component

Feedstock to the process consists of natural gas stream with dominant methane, carbon dioxide and steam stream. Products of the reforming process are consists of hydrogen, carbon dioxide and carbon monoxide plus traces of steam and unconverted hydrocarbon (methane slippage). Methane present as vapor at the reforming process. The pure component properties of the feedstock were listed in Table 4.1

Table 4.1: Physical property of the component at temperature 25°C and pressure 1 atm. (Airliquide, 2011)

Component	Molecular formula	MW (kg/kmol)	Boiling point, T_b (°C)	Density at T_b, ρ (kg/m^3)	Viscosity, η (cP)
Methane	CH_4	16.04	-161.5	1.819	0.0103
Water	H_2O	18.00	100.0	0.998	0.0097
Hydrogen	H_2	2.016	-252.8	0.0813	0.0086
Carbon dioxide	CO_2	44.01	-78.55	1.775	0.0140
Carbon monoxide	CO	28.01	-191.6	1.13	0.0180

To initialize the process and to can run the simulation, from specialty literature were chosen values for the proprieties of the gaseous phases implied in the reforming process. In the Table 4.2 is shown the initial condition of the streams, and the data subsequently optimized:

Table 4.2: The initial condition (CO_2 variation for study case).

Parameters	Natural gas	Steam
Temperature, C	450	450
Pressure, bar	40	40
Molar flow, kgmol/hr	1000	1500
Component	**Mole fraction**	
CH_4	1.00-0.88	0.00
H_2O	0.00	1.00
CO_2	0.00-0.12	0.00

4.1.2 Thermodynamic Property

In order to define the process, the thermodynamic property packages used to model both steady state and dynamic of methane must be specifies. The feed for the hydrogen production is considers relatively ideal mixture of methane, steam, carbon dioxide and carbon monoxide. In this approach, a model of Peng-Robinson Equation of State (EOS) is used to model the thermodynamics of hydrogen production for steady state operations.

This equation has been use to predict phase behavior for solutes with a wide range of volatility. In this method, it is assume that the solute in equilibrium with the saturated solution is a solid, which contains a negligible amount of the supercritical fluid substance. The partial molar volume *V* of the solid solute in the system at all the considered pressures and temperatures is equal to its molar volume at atmospheric pressure and 298K. The Peng-Robinson equation of state if given by:

$$p = \frac{RT}{V - b_1} - \frac{a_{11}(T)}{V^2 + 2Vb_1 - {b_1}^2}$$

(Equation 4.1)

where *R* is the gas constant, *T* is the absolute temperature, *V* is the molar volume of the pure solvent, *a* is a parameter describing attractive interactions between molecules, and *b* is a parameter describing volume exclusion and repulsive interactions. Subscript *1* represents the solvent and *2* represent the solute. Parameter *a* and *b* are determined from the critical properties of the components according to:

$$a = \frac{0.45724R^2{T_c}^2}{p_c}\left[1 + f(w)(1 - \sqrt{T_r})\right]^2$$

$$f(w) = 0.3744 + 1.54226w - 0.2699w^2$$

$$T_r = \frac{T}{T_c}$$

$$b = \frac{0.07780RT_c}{p_c}$$

(Equation 4.2)

Where T_c and P_c are the critical temperature and critical pressure, respectively, and *w* is the acentric factor. Thus the pure component parameters, *a* and *b* can be calculated as:

$$a_{11} = \frac{0.45724R^2{T_c}^2{}_1}{p_{c_1}}\left[1 + f(w_1)(1 - \sqrt{T_{r_1}})\right]^2$$

$$b_1 = \frac{0.07780RT_{c_1}}{p_{c_1}}$$

$$b_2 = \frac{0.07780RT_{c_1}}{p_{c_2}}$$

(Equation 4.3)

In order to calculate the properties of a mixture, a parameter k_{12} that describes the mixture must be introduced. The parameter k_{12} is called a binary interaction parameter and is included to account for the non-ideal of attraction between 1 and 2. In general, k_{12} should have a small positive value between 0 and 1. The binary interaction parameter is often adjusted to make the equation of state fit the experimental data. Therefore it can be derived as:

$$a_{11} = \frac{0.45724(1-k_{12})R^2T_{c1}T_{c2}}{\sqrt{p_{c_1}p_{c_2}}}\left[1+f(w_1)(1-\sqrt{T_{r_1}})\right]\left[1+f(w_2)(1-\sqrt{T_{r_2}})\right]$$

(Equation 4.4)

The Peng-Robinson equations for the mole fraction, x_2, at saturation of a solute of low volatility in a SCF can be written as:

$$ln\, x_2 = ln\left(\frac{p_v(T)}{p}\right) - ln\emptyset_2 + \frac{pV_m}{RT}$$

where p_v *(T)* is the vapour pressure of the solute, and V_m is the volume of the pure solute, and $\emptyset_2$ is the fugacity coefficient, it can be calculated to be given by

$$ln\, \emptyset_2 = ln\left(\frac{RT}{p(V-b_1)}\right) + \frac{b_1}{b_2}\left(\frac{pV}{RT}-1\right) - \left(\frac{a_{11}}{2\sqrt{2RTb_1}}\right)\left(\frac{2a_{12}}{a_{11}}-\frac{b_2}{b_1}\right) ln\left(\frac{V+(1+\sqrt{2})b_2}{V+(1+\sqrt{2})b_1}\right)$$

(Equation 4.5)

These equations allow the calculation of solubility at a given temperature and solvent molar volume, given the vapour pressure and molar volume of the state, the critical parameters and eccentric factors of both components and the binary interaction parameter. For dynamics modelling of hydrogen production, the Peng-Robinson Equation of state was found to simulate hydrogen production faster than the real time. When performing the dynamics simulation, Aspen HYSYS permits a user selected thermodynamics calculation procedure.

4.1.3 Integration Algorithm

A dynamic model is represented by a set of ordinary differential equation (ODEs) in Aspen HYSYS 2006. In order to solve the model, integration is required. The integration procedure must be started with a set of initial condition for each stable variable. There are three different varying step size integration method available in HYSYS; Euler, Runge-Kutta-Merson and Richard- Laming-Torrey. To provide a balance between accuracy and speed, Aspen HYSYS employs a unique integration strategy. The volume, energy and speed composition balances are solved at different frequencies. Volume balances are defaulted to solve at every integration step, whereas energy and composition balances are defaulted to solve at every 2nd and 10th integration step, respectively. The integration time step can be adjusted in Aspen HYSYS to increase the speed or stability of the system. The default value of 0.5 second was selected.

4.1.4 Mathematical Modeling of the Reactor Operation

The mathematical model of the system in the reformer is being develop based on two fundamental quantities, which is total mass balance and total energy balance. For N number of component in the system;

The overall material balance in the reformer:

$$\frac{dM_n}{dt} = \sum_{i=inlet} \rho_i F_i - \sum_{o=outlet} \rho_o F_o$$

(Equation 4.6)

With ρ is component density and F is component flow rate

The overall energy balance in the reformer:

$$\frac{d(h_n M_n)}{dt} = \sum_{i=inlet} \rho_i F_i c_i T_i - \sum_{o=outlet} \rho_o F_o \, c_o T_o$$

(Equation 4.7)

With h is the specific enthalpy, c is component heat capacity and T is temperature. By assuming $\frac{dh_n}{dt} \approx 0$, (the change in specific enthalpy is too small) and applying partial differential to the overall energy balance we got

$$h_n \frac{dM_n}{dt} = \sum_{i=inlet} \rho_i F_i c_i T_i - \sum_{o=outlet} \rho_o F_o \, c_o T_o$$

(Equation 4.8)

The overall mathematical model is developed:

$$h_n\left(\sum_{i=inlet} \rho_i F_i - \sum_{o=outlet} \rho_o F_o\right) = \sum_{i=inlet} \rho_i F_i c_i T_i - \sum_{o=outlet} \rho_o F_o \, c_o T_o$$

(Equation 4.9)

4.1.5 Degree of Freedom Analysis

There are two types of degree of freedom. The first one is dynamic degrees of freedom, N_m (m denotes manipulated). N_m is usually easily obtained by process insight as the number of independent variables that can be manipulated by external means. In general, this is the number of adjustable valves plus other adjustable electrical and mechanical devices. The second is steady state degrees of freedom, N_{ss} which is the number of variables needed to be specified in order for a simulation to converge. To obtain the number of steady state degrees of freedom we need to subtract from N_{om} which is the number of manipulated variables with no steady state effect and N_{oy} which is the number of variables that need to be controlled from N_m.

As a result Equation 4.10 is obtained

$$N_{ss} = N_m - (N_{om} + N_{oy})$$

(Equation 4.10)

In any process simulation work, it is essential that the degrees of freedom analysis be carried out to determine the number of variables to be specified.

4.1.6 Modeling and Simulation Assumption

Once the required equipment design parameters and thermodynamic-related properties have been set, the simulation can proceed when the initial conditions of each process stream is given. In running the simulation it is of great importance to ensure that proper initial values be used for each stream as failure in doing so may lead to convergence to different values, which is not desirable due to the non-linearity and unstable characteristics of the process. Once the initial conditions have been specified, iterative calculations are automatically performed until all the values in the calculated streams match those in the assumed stream within some specified tolerances. Assumption is needed in order to make our mathematical model a simple as possible. Several simplifying assumption that can usually be made are as follow:

1. The potential energy can always be ignored; the inlet and outlet elevations are roughly equal.
2. The inlet and outlet velocities are not high, therefore kinetic energy terms are negligible.
3. If there is no shaft work (no pump), W = 0.

Other assumptions can be made base on the reaction conditions and the equipments used.

4.2 Summary

This chapter is about the development of the simulation using Aspen HYSYS 2006 whereby all the data that collected from literature review is used. For the simulation of HYSYS, the equation of state that used is Peng-Robinson to calculate the stream physical and transport properties. Mass and energy balances have established for all cases. A brief summary about the simulation of hydrogen plant using Aspen HYSYS 2006 is shown in Figure4.1.

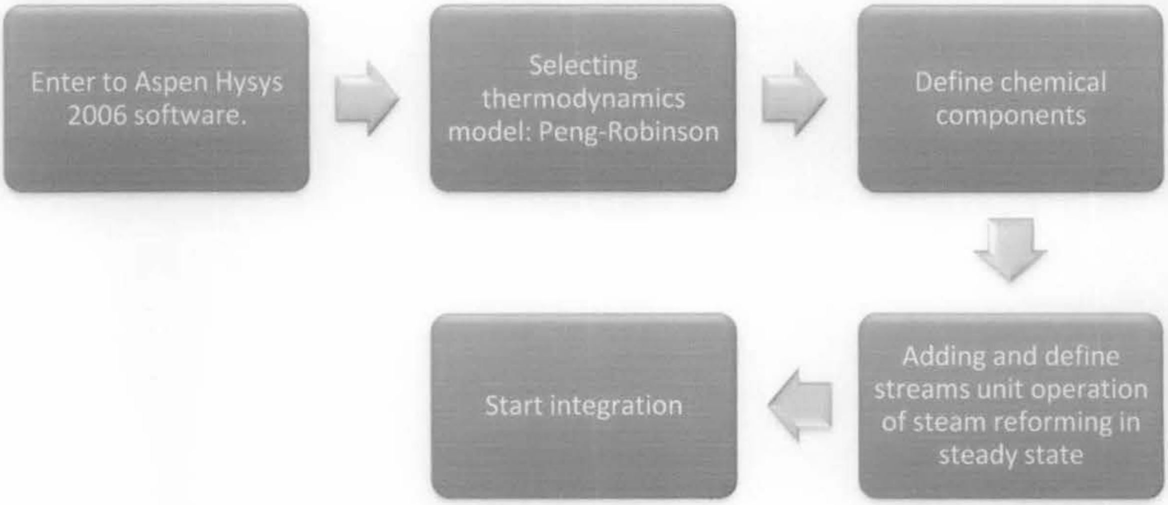


Figure 4.1: Block diagram of the simulation using Aspen HYSYS 2006

CHAPTER 5

RESULT AND DISCUSSION

5.1 Base case study

From the total reaction (Equation 3.3), the mole fraction ratio is 2 : 3 for methane over steam. Taking basis 1000 of kgmole/hr of reactant methane, the calculated molar flow rate for steam is 1500 kgmole/hr. Using this molar flow rate ratio, methane and water were fed into the single steam reforming unit. This reactor operated under gas phase and at 40 bar. All the raw materials are at temperature, 600°C and need to be heated-up by heater to reformer operating temperature, 850°C. The heating was needed for increasing the rate of reactions and for constant temperature feed into reactor.

The main objective of this steam reforming reactor is to produce hydrogen. However there still has some side products occurred in this reaction. Products such as unconverted methane can be eliminated by converting to hydrogen or carbon dioxide, while other products such as carbon monoxide, carbon dioxide and steam cannot be eliminated in this process. The treatment for reducing methane slippage will be discussed in next process later.

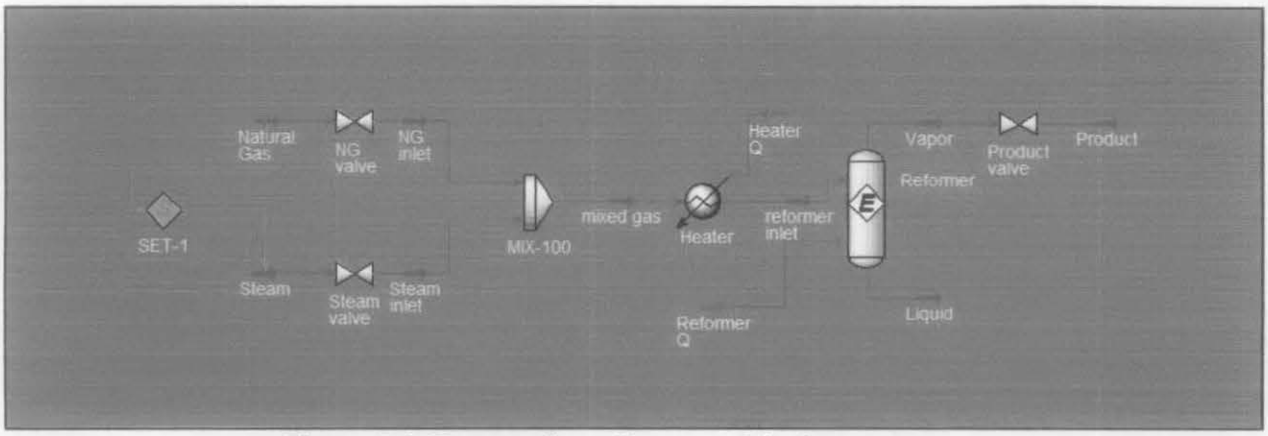


Figure 5.1: Process flow diagram of the base case.

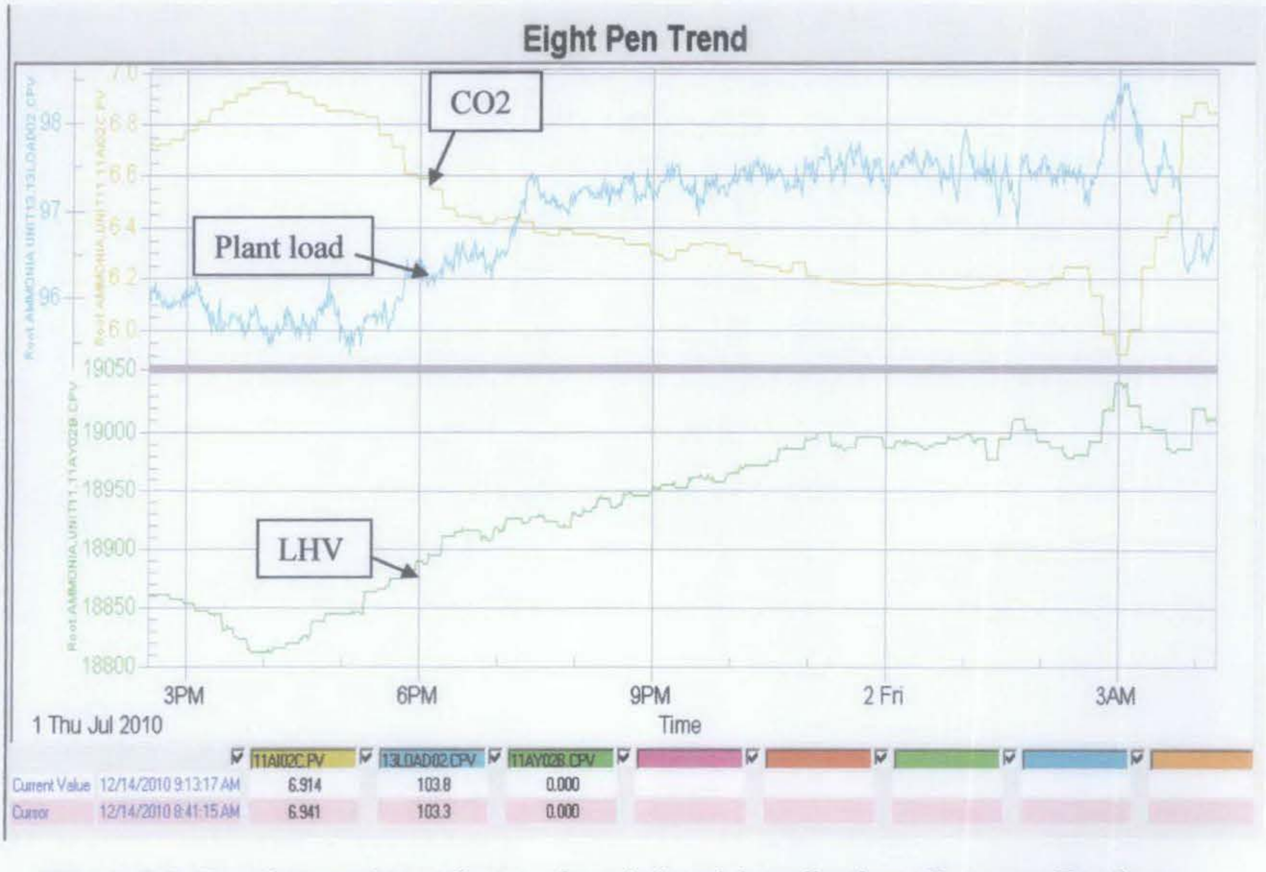
Figure 5.1 shows the process flow diagram of the base case developed using Aspen HYSYS 2006. From that figure, simulation development of hydrogen production from steam methane reforming was successful.

Table 5.1: Molar flow for components of effluent from steam reforming in case 1.

Component	Mole fraction	Molar flow (kgmole/hr)
Methane	0.1145	396.85
Hydrogen	0.4447	1541.33
Water	0.2667	924.38
Carbon dioxide	0.0612	212.39
Carbon monoxide	0.1126	390.27
TOTAL	1.000	3466.00

5.2 Base case validation

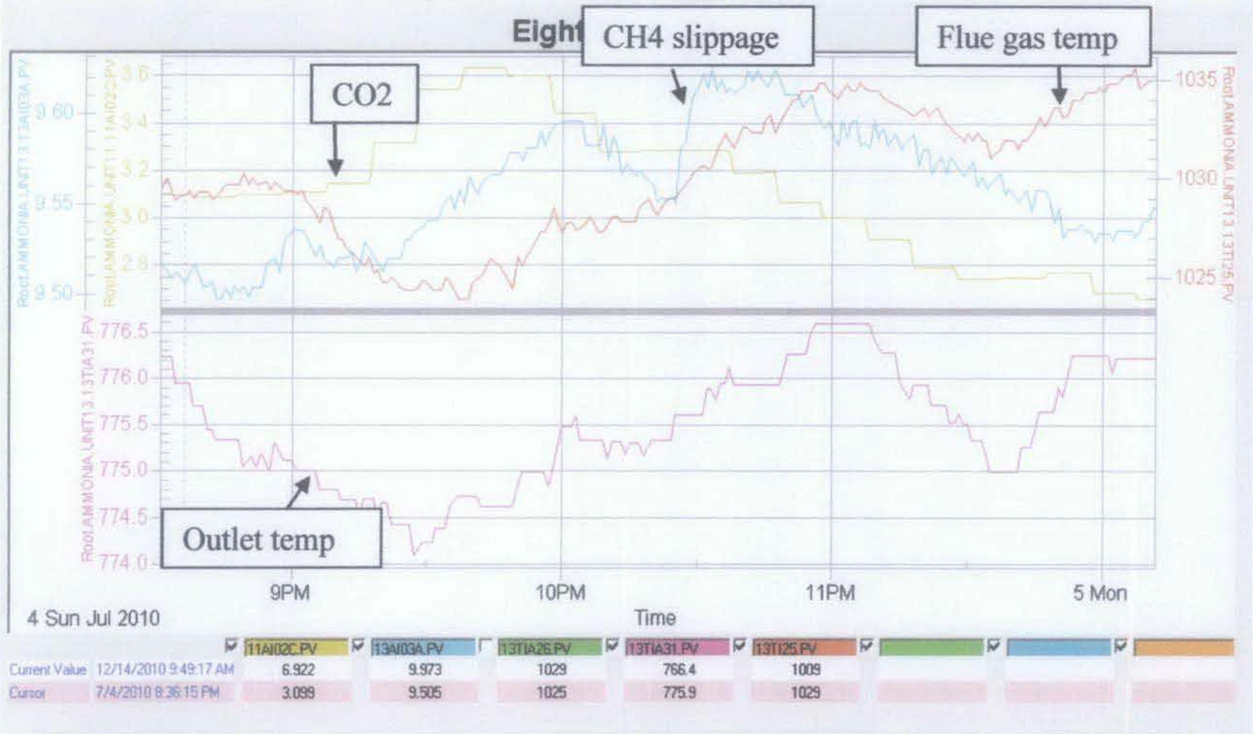
Validation was done by comparing the molar flow rate of the effluent by actual plant data from total reaction with the molar flow rate of the effluent of the steam reforming as simulated in Aspen HYSIS 2006 and also actual data from industrial application. In order to validate the reforming process model, variation of carbon dioxide in natural gas, flue gas temperature, methane slippage and outlet reformer temperature are compared with the actual plant data.



		☑ 11AI02C.PV	☑ 13LOAD02.CPV	☑ 11AY02B.CPV	☑	☑	☑	☑	☑
Current Value	12/14/2010 9:13:17 AM	6.914	103.8	0.000					
Cursor	12/14/2010 8:41:15 AM	6.941	103.3	0.000					

Figure 5.2: Trend on methane slippage from industrial application. *(Petronas Fertilizer Kedah, 2010)*

From the Figure 5.2, the data shown that variation of CO2 in natural gas would increase plant load. Increases of plant load shown in the figure would also increases the heating value (LHV) for sufficient heat reaction inside reformer.



		☑ 11AI02C.PV	☑ 13AI03A.PV	☐ 13TIA26.PV	☑ 13TIA31.PV	☑ 13TI25.PV	☑	☑	☑
Current Value	12/14/2010 9:49:17 AM	6.922	9.973	1029	766.4	1009			
Cursor	7/4/2010 8:36:15 PM	3.099	9.505	1025	775.9	1029			

Figure 5.3: Trend on methane slippage from industrial application. *(Petronas Fertilizer Kedah, 2010)*

From the Figure 5.3, the data shown that variation of CO2 in natural gas would increase the methane slippage. Increases of flue gas temperature shown in Figure 5.3 due to intervention by the operator to make sure outlet reformer temperature would not deviate with desired temperature.

The simulation results reveals of satisfactory fitness between data and the model although there are several differences. As been proved in the data, variation of CO2 would increase the methane slippage at outlet of the reformer due to poor heat transferred at reformer tube. All the figures shows the same condition as been discussed even data plotted are not suitable for comparison, but the concept is still the same. There is several critical conditions that leads to the contrary data, such as:

- The real condition of the plant would be different with the simulation data due to instrument malfunction during the data was taken.
- Inaccuracy of simulation model due to some process modification.
- Unavailability of proper data from plant due to restriction policy imposed by the company.

Therefore, the model developed using Aspen HYSYS 2006 was valid and can be used as a real process for further analysis.

5.3 Carbon dioxide variation on methane slippage

5.3.1 Evaluation on CO2 variation on natural gas.

The effect of CO2 variation on methane slippage has been tabulated in Table 5.2. Data from the simulation model, give a clear result that variation of carbon dioxide does have some effects on methane slippage and also to other components. For all cases, amount of methane and hydrogen are increased while other components such as water (steam), carbon dioxide and carbon monoxide are decreased. The data shown as increasing value of methane slippage even thought production of hydrogen also increasing.

Table 5.2: Composition of reformer effluent obtained from the HYSYS simulation.

Component	Case 1	Case 2	Case 3	Case 4
	Composition (mole fraction)			
Methane	0.1145	0.1188	0.1349	0.1403
Hydrogen	0.4447	0.4502	0.4701	0.4776
Water	0.2667	0.2619	0.2444	0.2377
Carbon dioxide	0.0612	0.0584	0.0484	0.0449
Carbon monoxide	0.1126	0.1106	0.1026	0.0994

5.3.2 Evaluation on reformer outlet temperature.

In Figure 5.4, the outlet methane composition yielded by reformer for all cases is plotted as a function of operating temperature of reformer. All cases are evaluated to determine relation operating temperature of reformer which favors low outlet methane composition based on the developed simulation model. As seen, the curve profiles are similar but there is a significant difference in case 1 and 4.

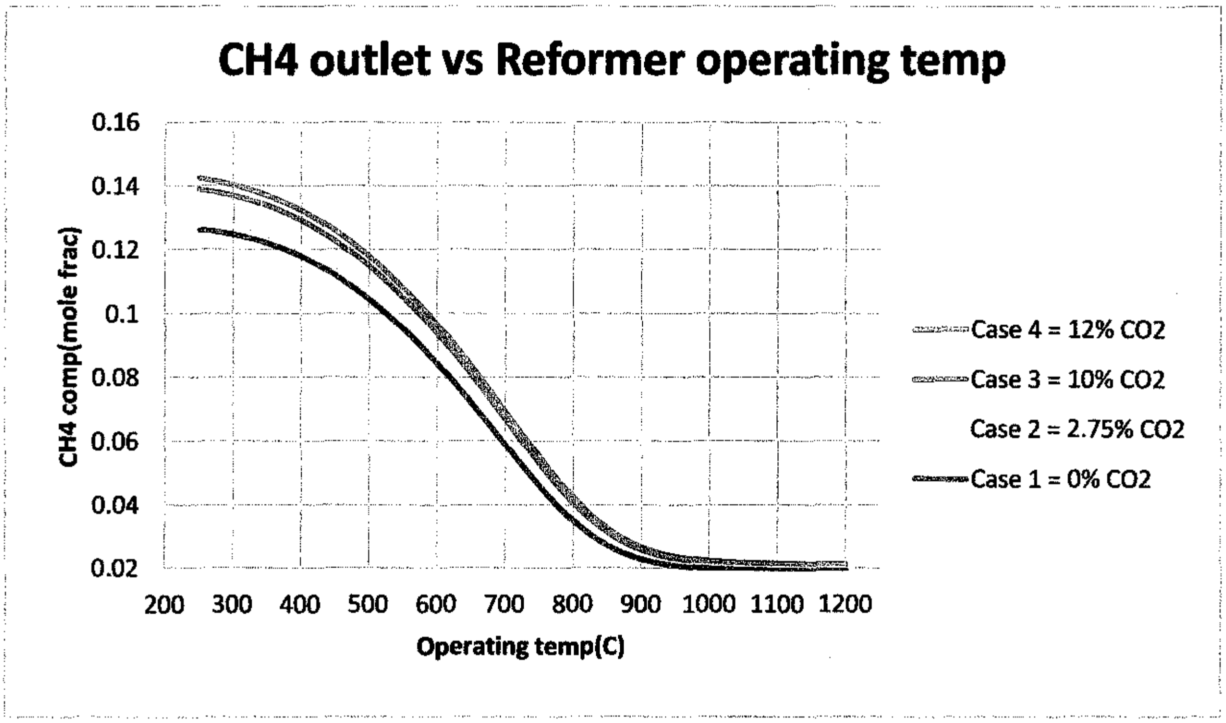


Figure 5.4: Relation on operating temperature region which favors low methane slip.

The difference outlet methane compositions on both cases are reduced when reformer operation temperature increases. As seen, outlet methane composition for all cases is reduced at final value, 0.02 mole fractions at operating temperature above 930°C. Its shows, when more heat being supplied to reformer outlet methane compositions (methane slippage) will decrease. Low composition of carbon dioxide in natural gas yielded less methane over increases temperature due to less hydrocarbon content in reformer. Thus, Figure 5.4 illustrated the operation temperature region at above 930°C would yield low methane slippage.

5.3.3 Evaluation on heat flow.

In Figure 5.5, the heat flow supplied to reformer for all cases is plotted as a function of operating temperature of reformer. All cases are evaluated to determine relation heat flow to reformer which favours low outlet methane composition based on the developed simulation model. As seen, the curve profiles are similar at temperature 500C but there is a significant difference in case 1 and 4.

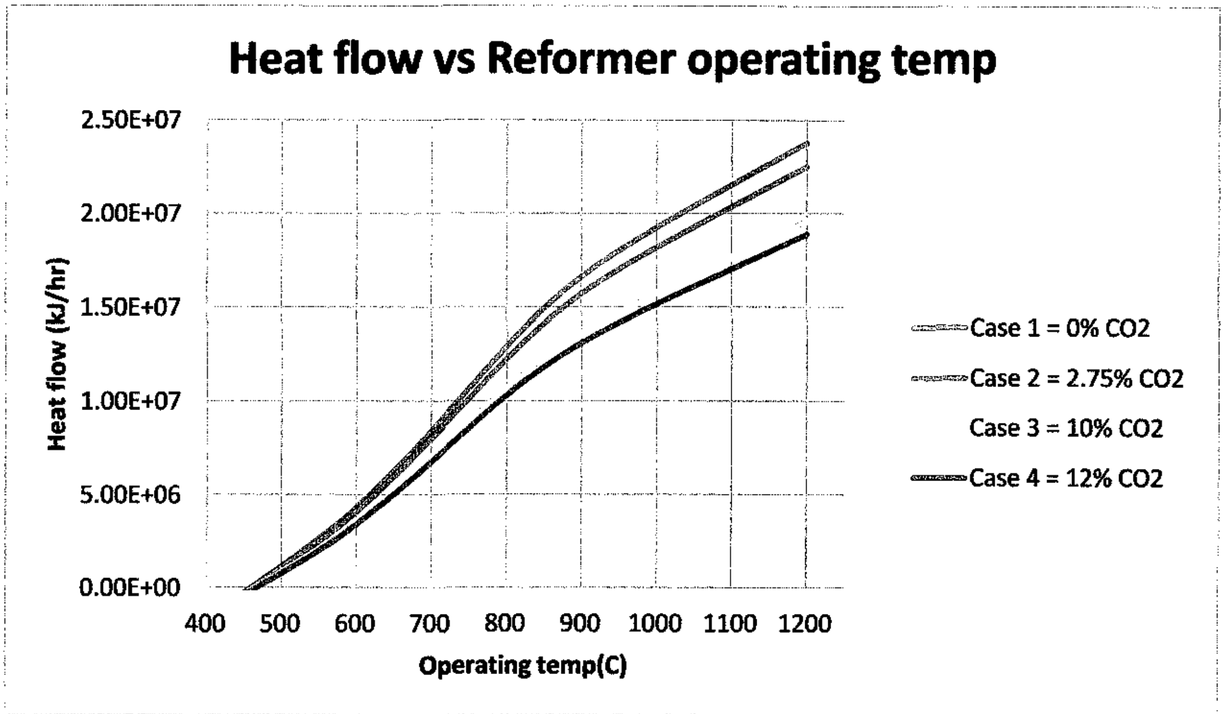


Figure 5.5: Relation on heat flow to operating temperature for all cases.

Figure 5.5 illustrates case 1 absorb more heat approximately 1.70×10^7 kJ/hr at 930C than case 4 at 1.40×10^7 kJ/hr at same operating temperature. This shows the high carbon dioxide composition in natural gas, heat supply by flue gas is decreases. Here, direct correlation of decreases heat flow to flue gas temperature drops is obtained by applying simple heat flow equation stated in below:

$$Q = mCp\Delta T \quad \text{(Equation 5.1)}$$

Where: Heat flow, Q in kJ/hr, heat capacity, Cp in kJ/kg.K, mass, m in kg and temperature difference between hot and cold side, ΔT in K. Assuming mass (m) and heat capacity of the product is constant. Based on the Equation 5.1, decreasing heat flow will leads to smaller temperature differences, (ΔT). When the heat flow decrease due to carbon dioxide composition fluctuation, less heat transferred into the reformer catalytic tube, less reforming reaction thus increases methane slippage at reformer outlet.

5.4 Reforming Efficiency

It is important to estimate the reforming process efficiency before the steam methane reforming plant being develop in real scale. The efficiency will determine either the reforming process can be profitable to develop or vice versa. In this research the efficiency of the reforming process are calculated using the formula shown below.

$$Efficiency, \% = \frac{(n_{H2}.LHV_{H2}) + (n_{CH4}.LHV_{CH4})}{(n_{natural\ gas}.LHV_{natural\ gas})} \times 100$$

with; n = molar flow rate, LHV = low heating value

The lower heating value (LHV) of H_2, CH_4 and natural gas are given (Lenz et al., 2005), while the other value are gained from the data results. In this study, with the hydrogen/methane ratio of 3.5 and steam/carbon ratio of 1.5, the calculated reforming process efficiency is about 45. 8% to 50.0% for four different cases simulated.

5.5 Summary

This chapter presents all the results obtained from the simulation of hydrogen production in steam methane reforming that was done in this research. Some discussion was carried out to explain the selection of certain value of parameters during the simulation process. The important part of this chapter is to present the final production of hydrogen and methane slippage and also the efficiency of the reforming process. Under this condition, the H_2yield is 44 mole% to 47 mole% and the reforming process efficiency is about 45. 8% to 50.0%..

CHAPTER 6

CONCLUSION AND REOMMENDATION

6.1 Summary

This study is conducted to stimulate methane slippage at hydrogen production plant using steam methane reforming. The simulation of the hydrogen production from steam methane reforming was carried out using computational software Aspen HYSYS 2006. There were two inputs for this process of hydrogen production which are methane and water (steam). In general, there were two reactions involved steam reforming, and methanation in this processes and methane slippage is observed at the reformer effluent. A fixed basis of 1000 kgmole/h methane was inserted to the process and the ratio molar flow for natural gas and water were obtained from the stoichiometry analysis using the overall reaction shown below.

$$2CH_4 + 3H_2O \rightarrow CO_2 + CO + 7H_2$$

The research methodology started with stoichiometry mathematical analysis, followed by base case development, base case validation, and lastly carbon dioxide variation on methane slippage. The variation of carbon dioxide composition in natural gas shows that it affects the reformer by increased methane slippage while also increase the hydrogen yield from the reformer. The important results of this research are the final production of hydrogen and methane slippage of all four cases, and the efficiency of the reforming process.

6.2 Conclusion

A number of important observations were noted based on the analysis of result as presented in the previous chapter. The main contributions of this research to the hydrogen production plant simulation on methane slippage are the following:

1. The effects of carbon dioxide composition in natural gas (feedstock), steam to carbon ratio (S/C) and reformer outlet temperature on methane slippage is observed and applied.
2. The hydrogen production plant was successfully developed using Aspen HYSYS 2006.
3. With the simulation data from all four cases, the fuel processor efficiency is 45.8% to 50.0%.

6.3 Recommendations

In the future works, it is recommended to study and integrate the following aspects:

1. Water Management

   The wet basis effluent of steam methane reforming still has a large significant of water vapor. This situation isn't ideal for lifespan of certain type of catalyst in reformer. Instead of wasting this effluent to the ambient, it is more efficient and economical to recycle this water back into the system to generate steam for reformer internal usage.

2. Dynamic state simulation

   The methane slippage at reformer effluent could be control by implementing low level process control. This can be also simulated in Aspen HYSYS by dynamic simulation.

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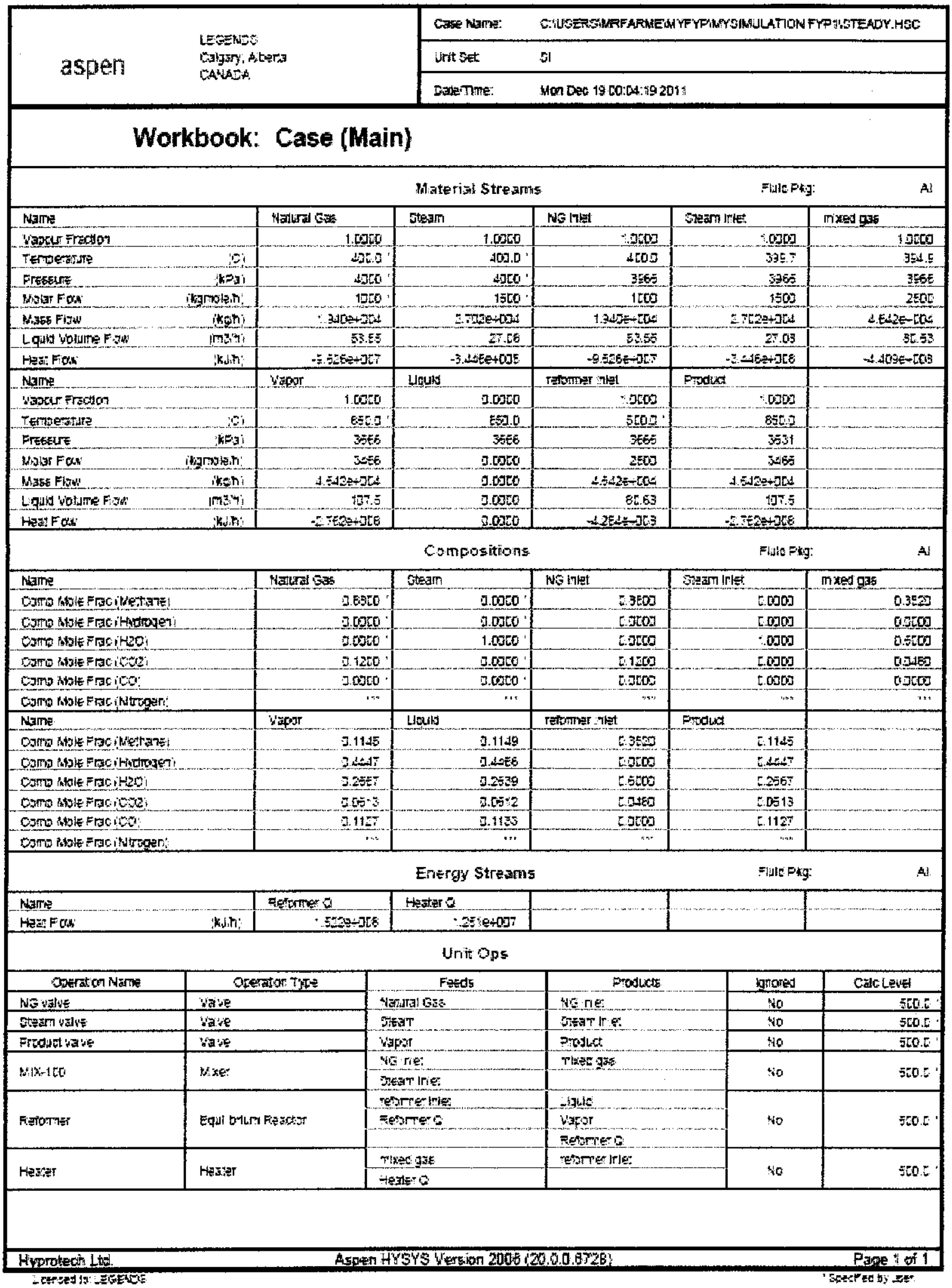
Appendix 1: Final Year Project 1 (May 2011) activities timeline

Activities in FYP1	**W1**	**W2**	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**	**W 10**	**W 11**	**W 12**	**W 13**	**W 14**	**W 15**	**W 16**	**W 17**
	15/5	**22/5**	**29/5**	**5/6**	**12/6**	**19/6**	**26/6**	**3/7**	**17/7**	**24/7**	**31/7**	**7/8**	**14/8**	**21/8**	**28/8**	**4/9**	**11/9**
Selection of project topic	▨	▨													**Study week**	**Final Examination Week**	**Final Examination Week**
Preliminary research work a) Literature review on simulation of steam methane reforming and methane slippage.		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨				
Submission of extended proposal defense						▨											
Proposal defense						▨	▨										
Project work continues b) Steady state simulation using Aspen HYSYS 2006. (Tutorial)																	
Submission of Interim Draft Report													▨				
Submission of Interim Report														▨			

Appendix 2: Final Year Project 2 (September 2011) activities timeline

Activities in FYP2	**W1**	**W2**	**W3**	**W4**	**W5**	**W6**	**W7**	**W8**	**W9**	**W10**	**W11**	**W12**	**W13**	**W14**	**W15**	**W16**	**W17**
	26/9	**3/10**	**10/10**	**17/10**	**24/10**	**31/10**	**7/11**	**14/11**	**21/11**	**28/11**	**5/12**	**12/12**	**19/12**	**26/12**	**31/12**	**9/1**	**16/1**
Project work continues b) Steady state simulation using Aspen HYSYS 2006. (Study cases)															**Study week**	**Final Examination Week**	**Final Examination Week**
c) Data validation with industry application, an ammonia plant																	
Submission progress report																	
Project work continues f) Report writing																	
Pre- SEDX											▨						
Submission of Draft Report																	
Submission of Dissertation (soft bound)																	
Submission of Technical Paper																	
Oral Presentation																	
Submission of Dissertation (hard bound)																	

Appendix 3: Data sheet for Case 1 from Aspen HYSYS simulation.



aspen

LEGENDS
Calgary, Alberta
CANADA

Case Name:	C:\USERS\MRFARME\MYFYP\MYSIMULATION FYP1\STEADY.HSC
Unit Set:	SI
Date/Time:	Mon Dec 19 00:04:19 2011

Workbook: Case (Main)

Material Streams — Fluid Pkg: All

Name		Natural Gas	Steam	NG Inlet	Steam Inlet	mixed gas
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000
Temperature	(C)	400.0 *	400.0 *	400.0	399.7	394.9
Pressure	(kPa)	4000 *	4000 *	3966	3966	3966
Molar Flow	(kgmole/h)	1000 *	1500 *	1000	1500	2500
Mass Flow	(kg/h)	1.940e+004	2.702e+004	1.940e+004	2.702e+004	4.642e+004
Liquid Volume Flow	(m3/h)	53.55	27.08	53.55	27.08	80.63
Heat Flow	(kJ/h)	-9.526e+007	-3.446e+008	-9.526e+007	-3.446e+008	-4.409e+008
Name		**Vapor**	**Liquid**	**reformer inlet**	**Product**	
Vapour Fraction		1.0000	0.0000	1.0000	1.0000	
Temperature	(C)	850.0 *	850.0	500.0 *	850.0	
Pressure	(kPa)	3666	3666	3666	3631	
Molar Flow	(kgmole/h)	3466	0.0000	2500	3466	
Mass Flow	(kg/h)	4.642e+004	0.0000	4.642e+004	4.642e+004	
Liquid Volume Flow	(m3/h)	107.5	0.0000	80.63	107.5	
Heat Flow	(kJ/h)	-2.762e+008	0.0000	-4.264e+008	-2.762e+008	

Compositions — Fluid Pkg: All

Name	Natural Gas	Steam	NG Inlet	Steam Inlet	mixed gas
Comp Mole Frac (Methane)	0.8800 *	0.0000 *	0.8800	0.0000	0.3520
Comp Mole Frac (Hydrogen)	0.0000 *	0.0000 *	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0000 *	1.0000 *	0.0000	1.0000	0.6000
Comp Mole Frac (CO2)	0.1200 *	0.0000 *	0.1200	0.0000	0.0480
Comp Mole Frac (CO)	0.0000 *	0.0000 *	0.0000	0.0000	0.0000
Comp Mole Frac (Nitrogen)	***	***	***	***	***
Name	**Vapor**	**Liquid**	**reformer inlet**	**Product**	
Comp Mole Frac (Methane)	0.1145	0.1149	0.3520	0.1145	
Comp Mole Frac (Hydrogen)	0.4447	0.4466	0.0000	0.4447	
Comp Mole Frac (H2O)	0.2567	0.2539	0.6000	0.2567	
Comp Mole Frac (CO2)	0.0513	0.0512	0.0480	0.0513	
Comp Mole Frac (CO)	0.1127	0.1133	0.0000	0.1127	
Comp Mole Frac (Nitrogen)	***	***	***	***	

Energy Streams — Fluid Pkg: All

Name		Reformer Q	Heater Q			
Heat Flow	(kJ/h)	1.502e+008	1.251e+007			

Unit Ops

Operation Name	Operation Type	Feeds	Products	Ignored	Calc Level
NG valve	Valve	Natural Gas	NG inlet	No	500.0 *
Steam valve	Valve	Steam	Steam Inlet	No	500.0 *
Product valve	Valve	Vapor	Product	No	500.0 *
MIX-100	Mixer	NG inlet Steam Inlet	mixed gas	No	500.0 *
Reformer	Equilibrium Reactor	reformer inlet Reformer Q	Liquid Vapor Reformer Q	No	500.0 *
Heater	Heater	mixed gas Heater Q	reformer inlet	No	500.0 *

Hyprotech Ltd. Aspen HYSYS Version 2006 (20.0.0.6728) Page 1 of 1

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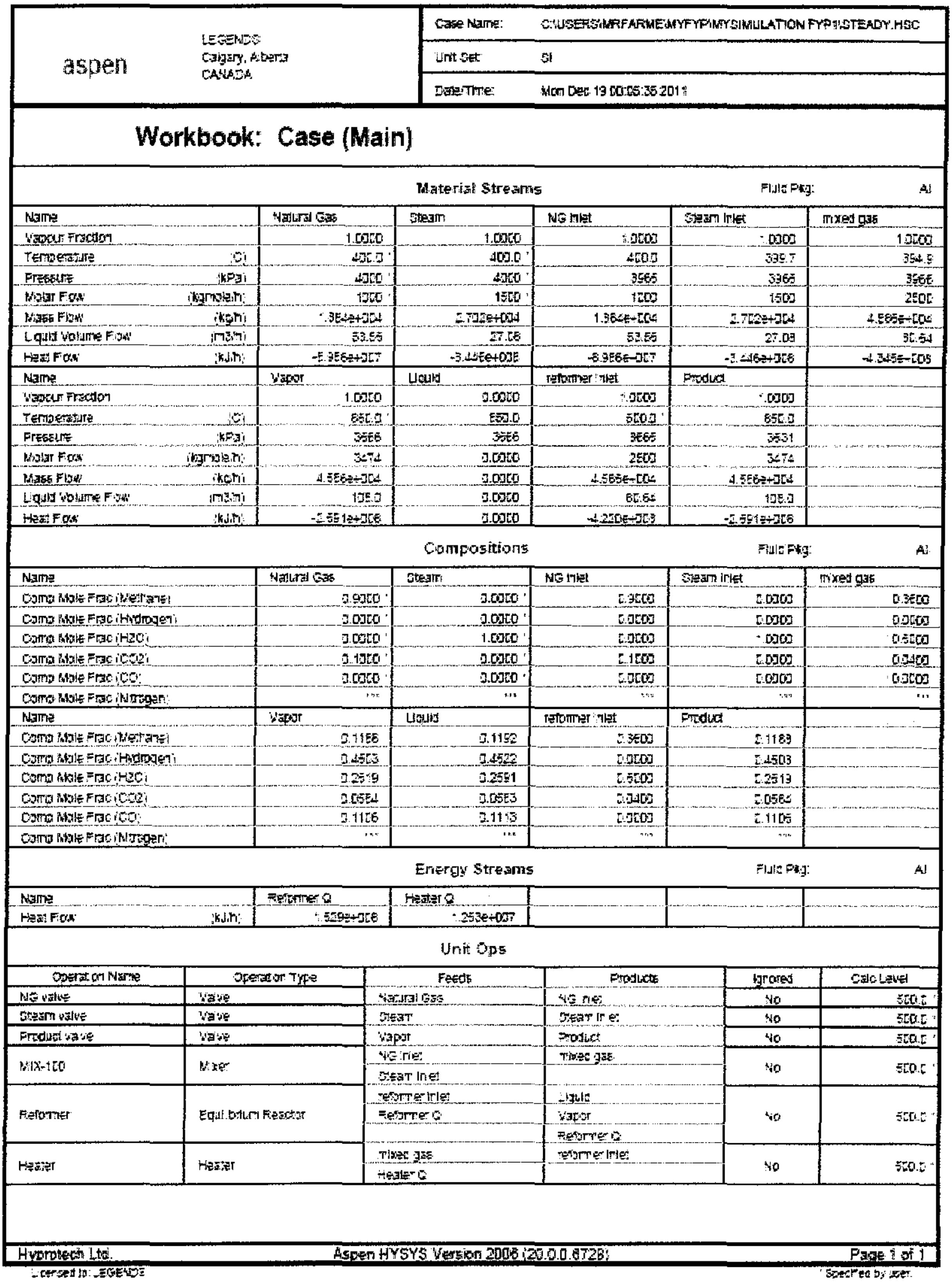
Appendix 4: Data sheet for Case 2 from Aspen HYSYS simulation.



aspen

LEGENDS
Calgary, Alberta
CANADA

Case Name:	C:\USERS\MRFARME\MYFYP\MYSIMULATION FYP1\STEADY.HSC
Unit Set:	SI
Date/Time:	Mon Dec 19 00:05:35 2011

Workbook: Case (Main)

Material Streams Fluid Pkg: All

Name		Natural Gas	Steam	NG Inlet	Steam Inlet	mixed gas
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000
Temperature	(C)	400.0 *	400.0 *	400.0	399.7	354.9
Pressure	(kPa)	4000 *	4000 *	3965	3965	3966
Molar Flow	(kgmole/h)	1000 *	1500 *	1000	1500	2500
Mass Flow	(kg/h)	1.864e+004	2.702e+004	1.864e+004	2.702e+004	4.566e+004
Liquid Volume Flow	(m3/h)	53.56	27.08	53.56	27.08	80.64
Heat Flow	(kJ/h)	-8.986e+007	-3.446e+008	-8.986e+007	-3.446e+008	-4.345e+008
Name		Vapor	Liquid	reformer inlet	Product	
Vapour Fraction		1.0000	0.0000	1.0000	1.0000	
Temperature	(C)	650.0 *	650.0	500.0 *	650.0	
Pressure	(kPa)	3566	3566	3665	3531	
Molar Flow	(kgmole/h)	3474	0.0000	2500	3474	
Mass Flow	(kg/h)	4.566e+004	0.0000	4.566e+004	4.566e+004	
Liquid Volume Flow	(m3/h)	105.0	0.0000	80.64	105.0	
Heat Flow	(kJ/h)	-2.591e+008	0.0000	-4.220e+008	-2.591e+008	

Compositions Fluid Pkg: All

Name	Natural Gas	Steam	NG Inlet	Steam Inlet	mixed gas
Comp Mole Frac (Methane)	0.9000 *	0.0000 *	0.9000	0.0000	0.3600
Comp Mole Frac (Hydrogen)	0.0000 *	0.0000 *	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0000 *	1.0000 *	0.0000	1.0000	0.6000
Comp Mole Frac (CO2)	0.1000 *	0.0000 *	0.1000	0.0000	0.0400
Comp Mole Frac (CO)	0.0000 *	0.0000 *	0.0000	0.0000	0.0000
Comp Mole Frac (Nitrogen)	***	***	***	***	***
Name	Vapor	Liquid	reformer inlet	Product	
Comp Mole Frac (Methane)	0.1166	0.1192	0.3600	0.1166	
Comp Mole Frac (Hydrogen)	0.4503	0.4522	0.0000	0.4503	
Comp Mole Frac (H2O)	0.2519	0.2591	0.6000	0.2519	
Comp Mole Frac (CO2)	0.0564	0.0563	0.0400	0.0564	
Comp Mole Frac (CO)	0.1106	0.1113	0.0000	0.1106	
Comp Mole Frac (Nitrogen)	***	***	***	***	

Energy Streams Fluid Pkg: All

Name		Reformer Q	Heater Q			
Heat Flow	(kJ/h)	1.629e+008	1.253e+007			

Unit Ops

Operation Name	Operation Type	Feeds	Products	Ignored	Calc Level
NG valve	Valve	Natural Gas	NG Inlet	No	500.0 *
Steam valve	Valve	Steam	Steam Inlet	No	500.0 *
Product valve	Valve	Vapor	Product	No	500.0 *
MIX-100	Mixer	NG Inlet Steam Inlet	mixed gas	No	500.0 *
Reformer	Equilibrium Reactor	reformer inlet Reformer Q	Liquid Vapor Reformer Q	No	500.0 *
Heater	Heater	mixed gas Heater Q	reformer inlet	No	500.0 *

Hyprotech Ltd. Aspen HYSYS Version 2006 (20.0.0.6728) Page 1 of 1

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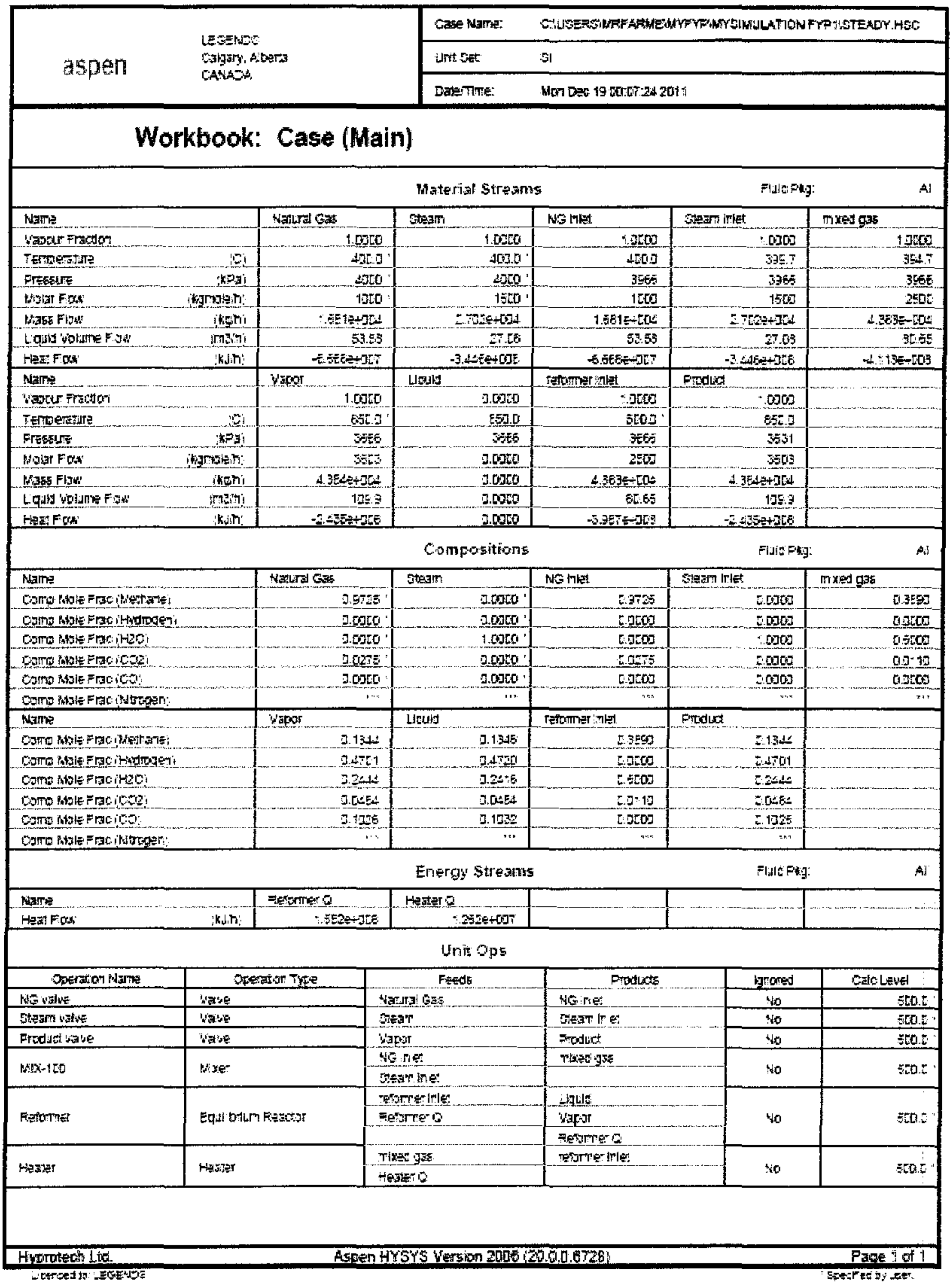
Appendix 5: Data sheet for Case 3 from Aspen HYSYS simulation.



aspen

LEGENDS
Calgary, Alberta
CANADA

Case Name:	C:\USERS\MRFARME\MYFYP\MYSIMULATION FYP1\STEADY.HSC
Unit Set:	SI
Date/Time:	Mon Dec 19 00:07:24 2011

Workbook: Case (Main)

Material Streams

Fluid Pkg: All

Name		Natural Gas	Steam	NG inlet	Steam inlet	mixed gas
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000
Temperature	(C)	400.0 *	400.0 *	400.0	395.7	354.7
Pressure	(kPa)	4000 *	4000 *	3965	3965	3965
Molar Flow	(kgmole/h)	1000 *	1500 *	1000	1500	2500
Mass Flow	(kg/h)	1.681e+004	2.702e+004	1.681e+004	2.702e+004	4.383e+004
Liquid Volume Flow	(m3/h)	53.58	27.08	53.58	27.08	80.65
Heat Flow	(kJ/h)	-6.666e+007	-3.446e+008	-6.666e+007	-3.446e+008	-4.113e+008

Name		Vapor	Liquid	reformer inlet	Product	
Vapour Fraction		1.0000	0.0000	1.0000	1.0000	
Temperature	(C)	850.0 *	850.0	500.0 *	852.0	
Pressure	(kPa)	3565	3565	3565	3531	
Molar Flow	(kgmole/h)	3503	0.0000	2500	3503	
Mass Flow	(kg/h)	4.384e+004	0.0000	4.383e+004	4.384e+004	
Liquid Volume Flow	(m3/h)	109.9	0.0000	80.65	109.9	
Heat Flow	(kJ/h)	-2.435e+008	0.0000	-3.987e+008	-2.435e+008	

Compositions

Fluid Pkg: All

Name	Natural Gas	Steam	NG inlet	Steam inlet	mixed gas
Comp Mole Frac (Methane)	0.9725 *	0.0000 *	0.9725	0.0000	0.3890
Comp Mole Frac (Hydrogen)	0.0000 *	0.0000 *	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0000 *	1.0000 *	0.0000	1.0000	0.6000
Comp Mole Frac (CO2)	0.0275 *	0.0000 *	0.0275	0.0000	0.0110
Comp Mole Frac (CO)	0.0000 *	0.0000 *	0.0000	0.0000	0.0000
Comp Mole Frac (Nitrogen)	***	***	***	***	***

Name	Vapor	Liquid	reformer inlet	Product	
Comp Mole Frac (Methane)	0.1344	0.1346	0.3890	0.1344	
Comp Mole Frac (Hydrogen)	0.4701	0.4720	0.0000	0.4701	
Comp Mole Frac (H2O)	0.2444	0.2416	0.6000	0.2444	
Comp Mole Frac (CO2)	0.0484	0.0484	0.0110	0.0484	
Comp Mole Frac (CO)	0.1026	0.1032	0.0000	0.1026	
Comp Mole Frac (Nitrogen)	***	***	***	***	

Energy Streams

Fluid Pkg: All

Name		Reformer Q	Heater Q			
Heat Flow	(kJ/h)	1.552e+008	1.262e+007			

Unit Ops

Operation Name	Operation Type	Feeds	Products	Ignored	Calc Level
NG valve	Valve	Natural Gas	NG inlet	No	500.0 *
Steam valve	Valve	Steam	Steam inlet	No	500.0 *
Product valve	Valve	Vapor	Product	No	500.0 *
MIX-100	Mixer	NG inlet Steam inlet	mixed gas	No	500.0 *
Reformer	Equilibrium Reactor	reformer inlet Reformer Q	Liquid Vapor Reformer Q	No	500.0 *
Heater	Heater	mixed gas Heater Q	reformer inlet	No	500.0 *

Hyprotech Ltd. Aspen HYSYS Version 2006 (20.0.0.6728) Page 1 of 1

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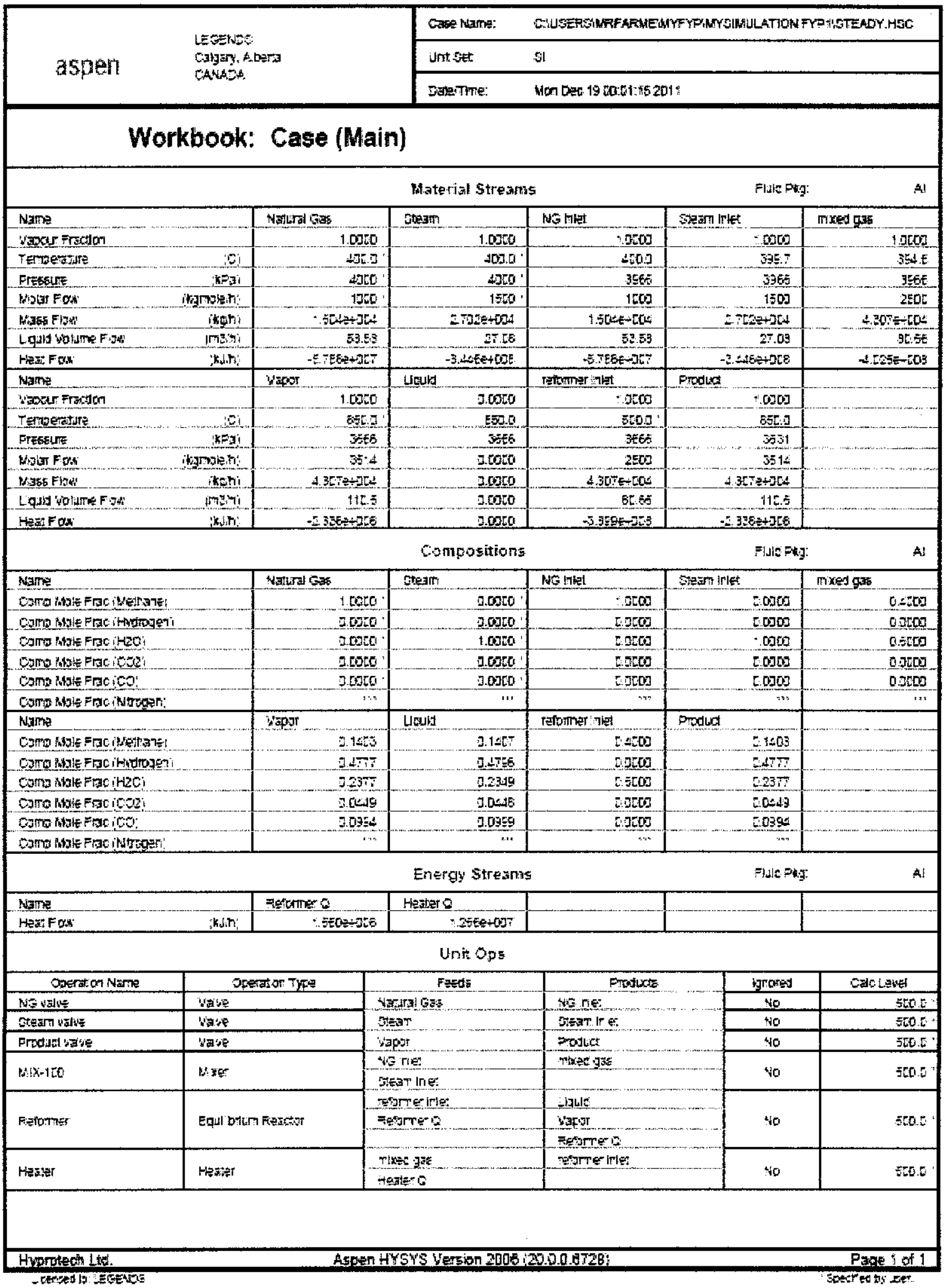
Appendix 6: Data sheet for Case 4 from Aspen HYSYS simulation.



aspen	LEGENDS Calgary, Alberta CANADA	Case Name:	C:\USERS\MRFARME\MYFYP\MYSIMULATION FYP1\STEADY.HSC
		Unit Set:	SI
		Date/Time:	Mon Dec 19 00:01:16 2011

Workbook: Case (Main)

Material Streams — Fluid Pkg: All

Name		Natural Gas	Steam	NG Inlet	Steam Inlet	mixed gas
Vapour Fraction		1.0000	1.0000	1.0000	1.0000	1.0000
Temperature	(C)	400.0 *	400.0 *	400.0	395.7	354.6
Pressure	(kPa)	4000 *	4000 *	3966	3966	3966
Molar Flow	(kgmole/h)	1000 *	1500 *	1000	1500	2500
Mass Flow	(kg/h)	1.604e+004	2.702e+004	1.604e+004	2.702e+004	4.307e+004
Liquid Volume Flow	(m3/h)	53.53	27.06	53.53	27.08	80.56
Heat Flow	(kJ/h)	-5.786e+007	-3.446e+008	-5.786e+007	-3.446e+008	-4.025e+008
Name		Vapor	Liquid	reformer inlet	Product	
Vapour Fraction		1.0000	0.0000	1.0000	1.0000	
Temperature	(C)	850.0 *	850.0	500.0 *	850.0	
Pressure	(kPa)	3966	3966	3966	3931	
Molar Flow	(kgmole/h)	3514	0.0000	2500	3514	
Mass Flow	(kg/h)	4.307e+004	0.0000	4.307e+004	4.307e+004	
Liquid Volume Flow	(m3/h)	110.5	0.0000	80.66	110.5	
Heat Flow	(kJ/h)	-2.336e+008	0.0000	-3.899e+008	-2.336e+008	

Compositions — Fluid Pkg: All

Name	Natural Gas	Steam	NG Inlet	Steam Inlet	mixed gas
Comp Mole Frac (Methane)	1.0000 *	0.0000 *	1.0000	0.0000	0.4000
Comp Mole Frac (Hydrogen)	0.0000 *	0.0000 *	0.0000	0.0000	0.0000
Comp Mole Frac (H2O)	0.0000 *	1.0000 *	0.0000	1.0000	0.6000
Comp Mole Frac (CO2)	0.0000 *	0.0000 *	0.0000	0.0000	0.0000
Comp Mole Frac (CO)	0.0000 *	0.0000 *	0.0000	0.0000	0.0000
Comp Mole Frac (Nitrogen)	***	***	***	***	***
Name	Vapor	Liquid	reformer inlet	Product	
Comp Mole Frac (Methane)	0.1403	0.1407	0.4000	0.1403	
Comp Mole Frac (Hydrogen)	0.4777	0.4756	0.0000	0.4777	
Comp Mole Frac (H2O)	0.2377	0.2349	0.6000	0.2377	
Comp Mole Frac (CO2)	0.0449	0.0446	0.0000	0.0449	
Comp Mole Frac (CO)	0.0954	0.0959	0.0000	0.0994	
Comp Mole Frac (Nitrogen)	***	***	***	***	

Energy Streams — Fluid Pkg: All

Name		Reformer Q	Heater Q			
Heat Flow	(kJ/h)	1.560e+008	1.266e+007			

Unit Ops

Operation Name	Operation Type	Feeds	Products	Ignored	Calc Level
NG valve	Valve	Natural Gas	NG Inlet	No	500.0 *
Steam valve	Valve	Steam	Steam Inlet	No	500.0 *
Product valve	Valve	Vapor	Product	No	500.0 *
MIX-100	Mixer	NG Inlet Steam Inlet	mixed gas	No	500.0 *
Reformer	Equilibrium Reactor	reformer inlet Reformer Q	Liquid Vapor Reformer Q	No	500.0 *
Heater	Heater	mixed gas Heater Q	reformer inlet	No	500.0 *

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