

**SIMULATION AND OPTIMIZATION OF GASOLINE AUTOTHERMAL
REFORMER FOR FUEL CELL APPLICATIONS**

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SIMULATION AND OPTIMIZATION OF GASOLINE AUTOTHERMAL
REFORMER FOR FUEL CELL APPLICATIONS

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A thesis submitted in partial fulfillment of the
requirements for the award of the degree of
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Faculty of Chemical and Natural Resources Engineering
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November, 2006

I declare that this entitle “Simulation and Optimization of Gasoline Autothermal Reformer for Fuel Cell Applications” is the result of my own research except as cited in the references. This thesis has not been accepted for any degree and is not concurrently submitted in candidate of other degree.

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To my beloved parents and my fiance

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ABSTRACT

Fuel cell systems are being developed for powering clean, efficient automobiles of the future. The proton exchange membrane fuel cell (PEMFC) systems being developed for such use require a fuel gas that is either pure hydrogen, or a gas mixture that contains significant concentration of hydrogen. Thus, the vehicles with gasoline as the on-board fuel use a fuel processor, also referred to as an autothermal reformer, to convert gasoline to a fuel gas and reformat, that contains hydrogen, carbon dioxide, water vapor, and nitrogen, with trace levels of other species, such as carbon monoxide and unconverted gasoline. With the help of Aspen HYSYS 2004.1 the steady state model has been developed to analyze the fuel processor and total system performance. In this case study, the PEM fuel cell system consists of the fuel processing and clean-up section, PEM fuel cell section and auxiliary units. While the fuel processing and clean-up section consists of Autothermal Reformer, High-temperature Shift, Medium-temperature Shift, Low-temperature Shift, and Preferential Oxidation. The purpose of this study is to identify the influence of various operating parameters such as A/F and S/F ratio on the system performance that is also related to its dynamic behaviours. From the steady state model optimization using Aspen HYSYS 2004.1, an optimised reaction composition, in terms of hydrogen production and carbon monoxide concentration, corresponds to A/F ratio of 18.5 and S/F ratio of 9.0. Under this condition, n-octane conversion of 100%, H₂ yield of 42% on wet basis and carbon monoxide concentration of 7.56ppm can be achieved. The fuel processor efficiency is about 80.41% under these optimised conditions.

ABSTRAK

Sistem sel bahan api sedang dibangunkan bagi tujuan memperolehi kuasa yang bersih dan sistem pengangkutan yang cekap untuk masa hadapan. Sistem elektrolit polimer sel bahan api (PEMFC) sedang dibangunkan bagi tujuan tersebut tetapi memerlukan hidrogen tulen atau campuran gas yang mengandungi kepekatan hidrogen pada kadar yang tertentu. Dengan demikian, kenderaan yang menggunakan gasolin sebagai bahan api yang diproses melalui *autothermal reforming* (ATR) telah dibangunkan. *Autothermal reforming* berfungsi untuk mengubah gasolin kepada gas bahan api dan bahan-bahan yang lain seperti hidrogen, karbon dioksida, wap air, dan gasolin yang tidak bertindak balas. Aspen HYSYS 2004.1 telah digunakan untuk membina model yang berkeadaan tetap, bagi menganalisa kecekapan pemproses bahan api dan keseluruhan sistem. Tujuan kajian ini adalah untuk mengenalpasti pengaruh bagi nilai-nilai berlainan operasi parameter terhadap pencapaian sistem yang juga berkait rapat dengan sifat-sifat dinamikinya. Di dalam kajian ini, sistem sel bahan api PEM terdiri daripada bahagian pemproses bahan api dan bahagian pembersihan, bahagian sel bahan api PEM dan unit-unit tambahan. Manakala, bahagian pemproses bahan api dan pembersihan pula terdiri daripada *Autothermal Reformer*, *High-temperature Shift*, *Medium-temperature Shift*, *Low-temperature Shift* dan *Preferential Oxidation*.. Daripada kajian yang telah dijalankan dengan menggunakan Aspen HYSYS 2004.1, nisbah A/F dan S/F adalah 18.5 dan 9.0 dimana penghasilan hidrogen dan kepekatan karbon monoksida adalah optimum. Di bawah keadaan ini, penukaran n-octane adalah 100%, penghasilan hidrogen sebanyak 42% dan kepekatan karbon monoksida adalah 7.56 ppm. Di samping itu, kecekapan pemproses bahan api adalah 80.41% dalam keadaan optimum ini.

TABLE OF CONTENTS

CHAPTER	TITLE	PAGES
	ACKNOWLEDGEMENTS	iv
	TABLE OF CONTENTS	vii
	LIST OF TABLES	xii
	LIST OF FIGURES	xiv
	LIST OF SYMBOL	xvi

CHAPTER I INTRODUCTION

CHAPTER I	INTRODUCTION	
	1.1 Introduction	1
	1.2 Problem Statement	4
	1.3 Objectives and Scope of Study	5
	1.4 Thesis Organizations	7

CHAPTER II
LITERATURE REVIEW

CHAPTER II LITERATURE REVIEW

2.1	Hydrogen production for fuel cells application	8
2.2	Hydrogen production for fuel cell application using gasoline	10
2.2.1	Hydrogen production for fuel cell applications using gasoline via steam reforming	11
2.2.2	Hydrogen production for fuel cell applications using gasoline via partial oxidation	14
2.2.3	Hydrogen production for fuel cell applications using gasoline via autothermal reforming	15
2.3	Steady state simulation of hydrogen production for fuel cell applications using gasoline	21
2.4	Summary	25

CHAPTER III METHODOLOGY

CHAPTER III METHODOLOGY

3.1	Research Tools	26
	3.1.1 Aspen HYSYS 2004.1	27
3.2	Research Activities	27
	3.2.1 Data Collection	27
	3.2.2 Steady State Model Development	29
	3.2.3 Steady State Model Validation	29
	3.2.4 ATR Optimization	30
	3.2.5 Heat Integration	30
	3.2.6 CO Clean up	31
	3.2.7 Plant wide optimization	31
3.3	Summary	32

CHAPTER IV STEADY STATE SIMULATION AND CONTROL OF HYDROGEN PRODUCTION FOR FUEL CELL APPLICATION

CHAPTER IV STEADY STATE SIMULATION AND CONTROL OF HYDROGEN PRODUCTION FOR FUEL CELL APPLICATION

4.1	Process Description of Hydrogen Production	
-----	--	--

	for Fuel Cell Application	33
4.2	Modelling and Simulation of Hydrogen Production for Fuel Cell Application	34
4.2.1	Physical Properties of the Pure Component	36
4.2.2	Thermodynamic Property	37
4.2.3	Integration Algorithm	39
4.2.4	Mathematical Modelling of the Reactor Operation	
4.2.4.1	Linear and Non-Linear Systems	40
4.2.4.2	Material Balance	41
4.2.4.3	Component Balance	43
4.2.4.4	Energy Balance	44
4.2.5	Pump Model	45
4.2.6	Mixer, Splitter (Tee) and Valve Models	46
4.2.7	Compressor	46
4.2.8	Expander	47
4.2.9	Furnaces	47
4.2.10	Cooler/Heater Model	48
4.2.11	Degree of Freedom Analysis	48
4.2.12	Steady State Simulation	49
4.3	Summary	50

CHAPTER V

RESULTS AND DISCUSSION

CHAPTER V RESULTS AND DISCUSSION

5.1	Base case simulation	51
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5.2	Validation	56
5.3	ATR optimization	58
5.4	Heat integration	61
5.5	CO clean up section	63
	5.5.1 Water-gas shift (WGS)	63
	5.5.2 Preferential oxidation (PROX)	66
5.6	Plant wide optimization	69
	5.6.1 CO clean up section – WGS	69
	5.6.2 CO clean up section- PROX	73
5.7	Temperature profile of fuel processor system	76
5.8	Molar fraction profile of fuel processor system	78
5.9	Process efficiency	80
5.10	Summary	81

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

CHAPTER VI CONCLUSIONS AND RECOMMENDATIONS

6.1	Summary	82
6.2	Conclusions	83
6.3	Recommendations	84

REFERENCES 86

APPENDIX A 95

LIST OF TABLES

NO. OF TABLES	TITLE	PAGES
2.1	The molecular formula, molecular weight, lower heating value, normal boiling point, latent heat of vaporization, and vapor heat capacity of these surrogate “compounds”	12
2.2	The characteristics of the processes for producing fuel-cell hydrogen from the standard fuels	13
2.3	The minimum reaction temperature required for avoiding coke formation	18
2.4	The investigated ranges of reformer conditions	22
2.5	Steam reforming based fuel processing, fuel cell, auxiliary and overall system efficiency	23
3.1	Chemical composition of the gasoline type hydrocarbon fuel	28
3.2	The investigated ranges of ATR conditions	28

4.1	The pure component properties of the part of the gasoline uses in this study	37
5.1	Component molar flow of the input and output stream of the ATR	55
5.2	Simulation results of the ATR using Aspen Hysys 2004.1	56
5.3	Error percentage between the calculated and simulated data	57
5.4	The results of the composition and conditions of ATR effluent and feed before and after optimization	60
5.5	Component molar flow of all components at CO clean up-WGS section before optimization	65
5.6	The composition of all components at LTS Vap stream and PEMFC In stream	68
5.7	The composition of the effluent of ATR, HTS, MTS and LTS before and after optimization	72
5.8	Comparison of the composition in PEMFC In before and after Optimization	75

LIST OF FIGURES

NO. OF FIGURE	TITLE	PAGES
2.1	Schematic diagram of the fuel reforming and clean-up sections	22
2.2	Principle of a scheme of an ATR process	24
3.1	Flowchart of the methodology	32
4.1	A schematic diagram of the fuel processing and clean –up section	33
4.2	HYSYS simulation environment	36
4.3	Reactor Operating	42
4.4	Stages in the simulation process	50
5.1	Process flow diagram of ATR	52
5.2	Influence of the air molar flow on the hydrogen, CO composition	

	and ATR outlet temperature	55
5.3	Process flow diagram of heat integration	61
5.4	Temperature profile of the heat integration	62
5.5	Process flow diagram of WGS	64
5.6	Process flow diagram of PROX	66
5.7	Influence of the water molar flow on the hydrogen production and CO concentration after entering WGS reactor	70
5.8	The relationship between water molar flows with HTS inlet temperature	71
5.9	Influence of the inject air molar flow in PROX on the CO concentration after entering PROX and PEMFC inlet temperature	74
5.10	Temperature profile of fuel processor system	77
5.11	Molar fraction profile of CO and hydrogen of fuel processor system	79

LIST OF SYMBOLS**NOMENCLATURE**

AFC	alkaline fuel cells
ATR	autothermal reforming
FCV	fuel cell vehicle
GHG	green house gases
HTS	high temperature water gas shift
ICE	internal combustion engines
LHV	lower heating value
LTS	low temperature water gas shift
MCFC	molten carbonate fuel cell
NRC	naphtha reforming catalyst

PAFC	phosphoric acid fuel cells
PEMFC	proton exchange membrane fuel cells
POX	partial oxidation
PROX	preferential oxidation
SOFC	solid oxide fuel cells
SPFC	solid polymer fuel cells
SR	stoichiometric ratio
SREF	steam reforming
TOX	total oxidation

CHAPTER I

INTRODUCTION

1.1 Introduction

Fuel cells, which have seen remarkable progress in the last decade, are being developed for transportation, as well as for both stationary and portable power generation. A variety of fuel cells for different applications is under development, e.g. solid polymer fuel cells (SPFC), also known as proton exchange membrane fuel cells (PEMFCs) operating about 353K, alkaline fuel cells (AFC) operating about 373K, phosphoric acid fuel cells (PAFC) about for 473K, molten carbonate fuel cell (MCFC) operating around 923K, solid oxide fuel cells (SOFC) for high temperature operation, 1073-1373K (Wang and Zhang, 2005).

The advances in fuel cells and their supporting technology have been spurred by the recognition that these electrochemical devices have the potential for both high efficiency and lower emissions. Automobile manufacturers have decided that, given the state of technology, the PEMFC has the best potential to replace the internal combustion engine for propulsion power. Their decision is based on many considerations, including

the ability to fit (size and weight) the power plant under the hood of the car, the ability to start up quickly, the ability to meet the changing power demands (dynamic response) typical in driving cycle, and cost (Ahmed and Krumpelt, 2005).

The fuel for the fuel cell system will vary with different applications. In transportation, it may be methanol, gasoline, or diesel. In stationary systems, it is likely to be natural gas, but it could also be propane. In certain niche markets, the fuel could be ethanol, butane, or biomass-derived materials. All these fuels are hydrocarbons or oxygenate that need to be reformed (Ahmed and Krumpelt, 2005). Partial oxidation (POX), autothermal reforming (ATR) and steam reforming (SREF) are the primary methods used in reforming hydrocarbons to produce hydrogen for use in PEM fuel cells.

Partial oxidation and autothermal reforming processes do not require indirect heating in contrast to steam reforming. Moreover, they offer faster startup time and better transient response. However, the product quality is poor due to low hydrogen concentrations, 70-80% for steam reforming versus 40-50% for partial oxidation and autothermal reforming on a dry basis. Compared with partial oxidation and autothermal reforming, catalytic steam reforming offers higher hydrogen concentrations. The steam reforming reaction on the other hand is a highly endothermic reaction and requires heating (Ersoz et al., 2006).

Majority the automobile manufacturers and oil industry accounts hydrogen as the ideal long-term fuel cell systems, but it is not yet clear, what will be the best fuel for the introduction of fuel cell systems. The use of hydrogen results in high efficiencies and a simple system design. Liquid fuels like methanol or gasoline on the other hand show advantages in terms of high energy density, easy fuel handling and-in the case of gasoline- in an existing fuel infrastructure (Wang and Zhang, 2005).

On board reforming of gasoline, which already presents a well-developed distribution network, is particularly interesting for a more efficient utilization of energy in vehicles, compared to internal combustion engines. Besides that, it also has the following advantages of higher heat value, large amounts of storage hydrogen and steady state supply as well as convenient transportation. Moreover, the method of producing hydrogen from gasoline through autothermal reforming combined of partial oxidation and steam reforming enjoys the merit of low energy requirement, due to the opposite contribution of the exothermic hydrocarbon oxidation and endothermic steam reforming (Wang and Zhang, 2005).

For the hydrogen production by gasoline reforming most researchers, prefer autothermal reforming concepts to steam reforming and partial oxidation because they enable

- a high hydrogen yield because of the addition of water to the feed
- minimization of NO_x – and soot-production by the addition of water and the low reaction temperatures (800-1000 °C)
- dynamic operation through in-situ provision of the required energy because of exothermal reactions.

The operating parameters of autothermal reformers are the stoichiometric ratio (SR) which is defined as the amount of oxygen in the feed divided by the amount of oxygen necessary for complete combustion and the feed temperature. In order to achieve high system efficiencies, a suitable system configuration was developed with the help of the steady state simulations (Aspen HYSYS 2004.1).

With respect to the above mentioned requirements there is also the need to optimise the dynamic behavior of a fuel cell system based on gasoline reforming. The quicker the system is able to follow load changes the smaller, cheaper and less heavy is the necessary battery in the car. For that purpose, the components of a fuel cell system

with autothermal reformer have to be described by appropriate dynamic simulation model. These models have to be implemented in a simulation program which is able to solve differential equations with the help of a numeric solver (Sommer et al., 2004).

1.2 Problem Statement

The amount and concentration of hydrogen generated from a given amount of gasoline, and the quality of the raw reformat (i.e. CO, CO₂, CH₄ and other hydrocarbons, H₂O, and N₂ contents), are influenced by the reforming conditions. The amount of H₂ produced determines the efficiency of the fuel processor; the greater this amount, the higher is the fuel processor efficiencies. Thus, this study will be covering the following area:

1. What are the optimum Air/Fuel (A/F) and Steam/Fuel (S/F) molar ratios to get the high hydrogen production with CO concentration less than 10 ppm?
2. What are the optimum A/F and S/F molar ratios to get the low inlet temperature of PEM fuel cell (70-80°C) with CO concentration less than 10 ppm?

1.3 Objectives and Scope of Study

The objective of this study is to find the optimum of A/F and S/F molar ratios of hydrogen production for fuel cell applications from gasoline via autothermal reforming. In order to achieve that objective, several scopes have been drawn:

1) Development of base case simulation

The base case simulation had been developed using the combined reforming of n-octane that involves a complex set of chemical reactions. From these parallel reactions, we got the stoichiometry of the n-octane ATR and calculate the input and output molar flow of the reformat.

2) Validation of base case model

At this stage, the output from the simulation will be compared with the results that from the base case simulation.

3) ATR optimization

The variations of operating parameters such as A/F molar ratios and temperatures will be using to investigate the influence to the hydrogen production and autothermal reformer efficiencies.

4) Heat integration

The heat integration process is very important in order to obtain the most economical reformer because the utilities cost can be reduce.

5) CO clean up

Whereas high temperature fuel cells (MCFC and SOFC) are capable of converting methane, CO and alcohols, etc. in the anode chamber by internal reforming, the PAFC and PEM cells do not tolerate excessive amounts of CO. The PEMFC does not tolerate

more than in the order of 50 ppm CO; the lower the CO concentration, the higher the efficiency of the cell.

5.1) WGS

The water gas shift reaction is an inorganic chemical reaction in which water and carbon monoxide react to form carbon dioxide and hydrogen (water splitting). This reaction will reduce the amount of CO besides of producing hydrogen.

5.2) PROX

The preferential oxidation is a parallel reaction in which CO and oxygen react to form carbon dioxide while hydrogen and oxygen react to form water.

6) Plant wide optimization

6.1) WGS

The variations of S/F molar ratios will be using to investigate the influence of these parameters to hydrogen production, temperature and CO concentration.

6.2) PROX

The variations of air that will be injecting to PROX will be using to investigate the influence to the hydrogen production, temperature entering the fuel cell and CO concentration.

1.4 Thesis Organizations

The important of this study is to identify potential design issues and obtain preliminary estimate of the expected system efficiency. So, the simulation of a gasoline autothermal reforming had been constructed in order to identify the autothermal reforming operating conditions and their effect on the overall system performance or efficiency. Therefore, the objective of this study is to simulate and optimize a gasoline autothermal reformer for fuel cell applications using Aspen HYSYS 2004.1. The remainder of this paper is organized as follows, Chapter II describes the literature review of this study and the methodology of this research was described at Chapter III. Chapter IV and Chapter V discussed about steady state simulation of hydrogen production and results and discussion. Lastly, the conclusion and recommendations for future works are drawn in Chapter VI.

CHAPTER II

LITERATURE REVIEW

2.1 Hydrogen production for fuel cells application

There are a lot of research have been done in hydrogen production using different feed and different process reforming. There are a lot of inputs that can be used in hydrogen production such as methane, butane, propane, ethane, methanol, propanol, gasoline, diesel and jet fuel (Springmann et al., 2002).

Hydrogen production from methane has been discussed by Silva et al. (2002), Suelves et al. (2004), Ferna'ndez et al. (2005), Hamid et al. (2006) and Hoang et al. (2006). At present, steam reforming of natural gas (SMR) is the most widespread method to produce hydrogen. However, a critical review of the well to wheel studies carried out by different institutions shows that the green house gases (GHG) reduction derived from using SMR-Hydrogen in fuel cell vehicle (FCV) instead of compressed natural gas in internal combustion engines (ICE) could not be high enough to justify the dramatic hangs needed to move from ICE to FCV. That is due to the high GHG

emissions in hydrogen production by SMR. These emissions have to be drastically reduced in order to realize the GHG depletion claimed for the transition to FCV (Suelves et al., 2004).

Hydrogen production from butane have been discussed by Soo et al. (2006), Laisiripojana et al. (2005), Avci et al. (2004), Chen et al. (2004), Ersoz et al. (2003) and Frias et al. (2003).

Hydrogen production from propane have been discussed by Aartun et al. (2005), Yi et al. (2005), Ersoz et al. (2003), Mizuno et al. (2003), Avci et al. (2001), Hey et al. (2000), Grosjean et al. (2004)

Hydrogen production from ethane have been discussed by Soo et al. (2006), Hoang et al. (2006), Navarro et al. (2006), Laosiripojana et al. (2005), Aartun et al. (2005), Kusakabe et al. (2005), Qijan et al. (2005), Shetian et al. (2005) and Linsheng et al. (2003).

Hydrogen productions from methanol have been discussed by Shetian et al. (2006). They study about the hydrogen production by oxidative methanol reforming. Fukahori et al. (2006) described about the methanol steam reforming over paper like composites of Cu/ZnO catalyst and ceramic fiber. Reuse et al. (2004) have reported on hydrogen production with SR using methanol in an auto thermal micro-channel reactor. Besides of the research that stated above, there are much more research that been done by Feg et al. (2006), Cheng et al. (2006), Constantino et al. (2005), Ya et al. (2005), Gu et al. (2005), Erickson et al. (2004), Peters et al. (2000) and Wiese et al. (1999).

For the hydrogen production using propanol, Shoko et al. (2006), Resini et al. (2006), Wang et al. (2005), Xinhai et al. (2005), Mattos et al. (2005), Fernandez et al.

(2005), Yi et al. (2005), Barbir (2005), Avci et al. (2004) and Mizuno et al. (2003) have discussed about it.

Jet fuel is also one of the feed that can be reforming to produce hydrogen. Brown (2001) has done the research on a comparative study of fuels for on-board hydrogen production for fuel-cell-powered automobiles. Steam reforming of kerosene on Ru/Al₂O₃ catalyst to yield hydrogen has been discussed by Suzuki et al. (2000). Dagaut et al. (2006) studied on the combustion of kerosene using 1- to 3-component surrogate model fuels. Reference components of jet fuels from kinetic modeling and experimental results discussed by Agosta et al. (2004), while direct oxidation of jet fuels and Pennsylvania crude oil in a solid oxide fuel cell has been studied by Zhou et al. (2004).

2.2 Hydrogen production for fuel cell applications using gasoline

There are a lot of research that had been carried out with several approaches to produce hydrogen using gasoline such as steam reforming (SREF), electrochemical, photochemical, biological, and thermochemical methods (Wang and Zhang, 2005). Although numerous technologies exist for producing hydrogen, the three main methods are steam reforming (SREF), auto thermal reforming (ATR), and partial oxidation (POX, also known as rich combustion) (Mjaanes et al., 2005).

2.2.1 Hydrogen production for fuel cell applications using gasoline via steam reforming

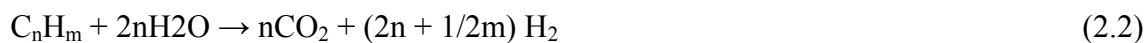
SREF is an endothermic process leading to hydrogen, carbon monoxide and carbon dioxide and is catalysed by nickel or noble metal catalysts (Springmann et al. 2002). Steam reforming is one of the least expensive hydrogen production methods (Wang and Zhang, 2005). Furthermore, it is able to produce high hydrogen concentration in the reformed gas, about 70%. Therefore the efficiency of hydrogen production is high. However, the steam supply of the reactor is a problem for mobile system (Minutillo, 2005). The fuel cell performance is progressively degraded by CO poisoning of Pt anode catalyst. Therefore, CO conversion processes such as high temperature water gas shift (HTS), low temperature water gas shift (LTS) reactions, and/or preferential partial oxidation are required to reduce the CO concentration within the tolerance limit of the Pt anode catalyst (Dong et al., 2001).

Brown (2001) has reported on comparison of seven common fuels for their utility as hydrogen sources for proton-exchange-membrane fuel cells used in automotive propulsion. Methanol, natural gas, gasoline, diesel fuel, aviation jet fuel, ethanol, and hydrogen are the fuels considered. Unlike methane and methanol, gasoline, diesel fuel, and aviation jet fuel are not single compounds. These latter fuels consist of numerous components, and are obtained by processing crude oil in petroleum refinery. Table 2.1 presents the molecular formula, molecular weight, lower heating value, normal boiling point, latent heat of vaporization, and vapor heat capacity of these surrogate “compounds”.

Table 2.1: The molecular formula, molecular weight, lower heating value, normal boiling point, latent heat of vaporization, and vapor heat capacity of these surrogate “compounds”. (Brown, 2001)

Fuel	Molecular formula of surrogate	Molecular weight of surrogate	LHV of surrogate (kJ/mol)	b.p. of surrogate (°C)	ΔH_{vap} of surrogate (kJ/mol)	Cp of surrogate vapor (J/mol K)
Gasoline	$C_{7.14}H_{14.28}$	100	4270	100	31	180
Aviation jet fuel	$C_{15}H_{30}$	210	9030	245	50	370
Diesel fuel	$C_{13.57}H_{27.14}$	190	8080	230	47	340

The general expression for the reaction of steam with hydrocarbons is:



Steam-reforming of gasoline:



Table 2.2 gives some characteristics of the processes for producing fuel-cell hydrogen from the standard fuels considered in this work. It presents temperatures of the

processes initial reactions, the carbon monoxide amounts in the outlet streams from the initial reactions, and the theoretical input energies for the processes. These characteristics are important in judging the utility of these fuels for on-board generation of fuel-cell hydrogen for automotive propulsion.

Table 2.2: The characteristics of the processes for producing fuel-cell hydrogen from the standard fuels. (Brown, 2001)

Process	CO in product (mol% or vol %)	Temperature range (K)	Total theoretical input energy
<i>Steam reforming of</i>			
Methane	11.2	1000-1100	0.141
Methanol	0.8	500-560	0.145
Ethanol	10.0-14.0	800-1000	0.144
Gasoline, diesel fuel, and aviation jet fuel	20.0	1000-1150	0.148
<i>Partial oxidation of</i>			
Methane	20.0	1500-1600	0.147
Gasoline, diesel fuel, and aviation jet fuel	25.0	1150-1900	0.169

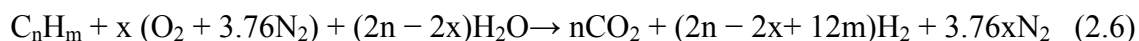
2.2.2 Hydrogen production for fuel cell applications using gasoline via partial oxidation

POX is known as the conversion of hydrocarbons with substoichiometric supply of oxygen. Depending on the oxygen ratio λ which $\lambda = 1$ corresponds to complete combustion to carbon dioxide and steam (Springmann et al., 2002). POX of hydrocarbons can be thermally neutral to strongly exothermic. Partial oxidation needs external cooling and generates a high concentration of CO, which is not desired for fuel cell applications (Biniwale, et al., 2004). The POX reaction can either be run with or without catalysts. Catalytic POX reactions at high temperature are very fast and tend to be mass transfer limited (Springmann et al, 2002). One of the most promising non-catalytic partial oxidation techniques is combustion inside a porous medium. This medium could be a fluidized or a stationary bed. In a fluidized bed system, the incoming velocity of the gases is high enough to lift the particles. A spouted-bed combustor involves motion of solid inert (or catalytic) particles in a recirculatory manner; this technique has been used to stabilize rich flames of methane in order to produce syngas (Mjaanes et al., 2005).

Dong et al. (2001) have reported on the partial oxidation reforming (POX or autothermal reforming, ATR) reaction of iso-octane with/without 100 ppm sulfur and of reformulated naphtha over a commercial naphtha reforming (NRC) catalyst. This is as part of the development of gasoline reforming system for integration with proton exchanged membrane (PEM) fuel cell. Due to the favorable factors required for the on board generation of H₂ in the fuel cell vehicles, POX reforming (or auto thermal reforming, ATR) of gasoline attracts much attention primarily because of a low energy requirement. The fuel cell performance is progressively degraded by CO poisoning of Pt anode catalyst. Therefore, CO conversion processes such as high temperature water gas shift (HTS), low temperature water gas shift (LTS) reactions, and/or preferential partial oxidation are required to reduce the CO concentration within the tolerance limit of the Pt anode catalyst. The following POX reactions will be considered:



The overall POX reforming reaction of iso-octane in gasoline fuel processor is given by:



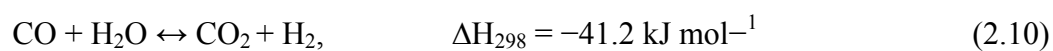
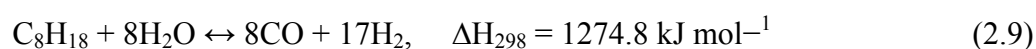
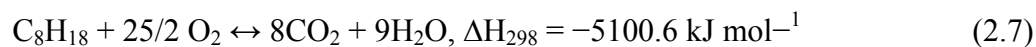
Where x is a ratio of oxygen/fuel.

2.2.3 Hydrogen production for fuel cell applications using gasoline via auto thermal reforming

Combining SR and POX a reformer can be operated auto thermally. The heat necessary for SR is provided by the oxidation of a part of the hydrocarbon fuel. ATR seem to be the most promising concept for mobile applications because the reactor design is much simpler (smaller and lighter unit), than that of conventional steam reformer with internal heat exchanger. Argonne National Laboratory (ANL) has actively studied catalytic ATR process to utilize hydrocarbon fuels for fuel cell transportation applications (Lee et al., 2005). It also has received much research and development attention as a viable process for hydrogen generation for fuel-cell systems because it offers advantages of lower operating temperature (easier start-up and a wider choice of materials), and flexible load following characteristic as compared to the SREF process. It also has higher energy efficiency than the POX process (Lee et al., 2005).

When SR and POX react simultaneously, the reformer efficiency also increases. Besides that, the dynamic behavior is expected to be very good, which is important for mobile application (Springmann et al., 2002). Moreover, the feed stoichiometry can be tuned to adapt to cold start or changes in the power demand. The appropriate choice of O/F and S/F ratios also allows the reaction to proceed without external heating. Important parameters for the reaction are temperature, pressure, O/F and S/F molar ratios. These parameters should be chosen with the aim of avoiding the formation of carbonaceous deposits, and of optimizing hydrogen production, hydrocarbon conversion and H₂ + CO selectivity (Villegas et al., 2005).

Trimm et al. (2004) have done the research on the autothermal reforming of model gasoline mixtures to produce hydrogen for fuel cell. The production of hydrogen from methane, methanol and light hydrocarbons has been reported. This present studies are focused on the conversion of model hydrocarbons typical of gasoline, e.g.



From the results observed, although hydrogen yields and selectivity were higher with higher S/F ratios, the extra weight to be carried by the vehicle would reduce fuel consumption. However, lower S/F ratios do produce sufficient hydrogen for fuel cell operation. The production of carbon monoxide is too high for fuel cells, and selective removal of the potential poison will be required.

Rajesh et al. (2004) discussed about the iso-octane that has been used to simulate the reforming of gasoline under autothermal conditions using a S/F ratio equal to 1 and an equivalence ratio equal to 0.32. Autothermal reforming is considered a better option for hydrocarbon conversion to hydrogen-rich gas because it provides hydrogen rich gas with lower concentrations of CO. It has been carried out at different temperature with certain catalysts supported on alumina mesh. A novel spray-pulsed reactor with fine nozzle is used for providing atomized iso-octane in pulses.

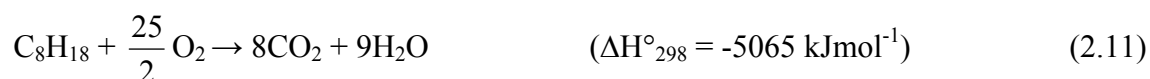
In this article, the minimum reaction temperatures required for avoiding coke formation during iso-octane reforming at thermodynamic equilibrium is also included. The reaction temperatures required to prevent the formation of coke during reforming of iso-octane at thermodynamic equilibrium have been compared as shown in Table 2.3. For partial oxidation (POX) the temperature is 1180°C, 1030°C for autothermal reforming (ATR), and 950°C for steam reforming (SREF). This is for O/F molar ratio equal to 1.

Table 2.3: The minimum reaction temperature required for avoiding coke formation
(Rajesh et al., 2004)

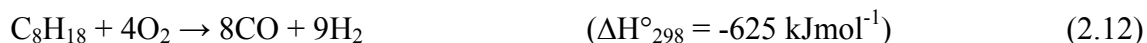
Reactants	Type of reaction	O/F molar ratio	Min. T required for avoiding coke formation (°C)
$C_8H_{18} + 4(O_2 + 3.76N_2)$	POX	1	1180
$C_8H_{18} + 2(O_2 + 3.76N_2) + 4H_2O$	ATR	1	1030
$C_8H_{18} + 8H_2O$	SREF	1	950
$C_8H_{18} + 4(O_2 + 3.76N_2) + 8H_2O$	ATR	2	575
$C_8H_{18} + 16H_2O$	SREF	2	225

Villegas et al. (2005) have done the research on a combined thermodynamic or experimental study for the optimization of hydrogen production by catalytic reforming of isooctane. Catalyst that used is Pt catalyst supported on a CeO₂-ZrO₂ mixed oxide support. The combined reforming of isooctane involves a complex set of chemical reactions. The primary reactions lead to the decomposition of the hydrocarbon, while many secondary reactions may also take place between the different products together and with steam.

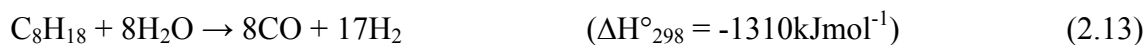
Total oxidation:



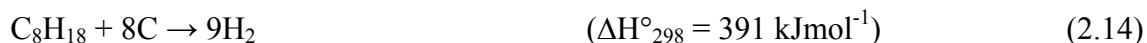
Partial oxidation:



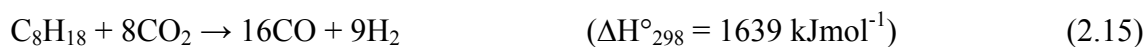
Steam reforming:



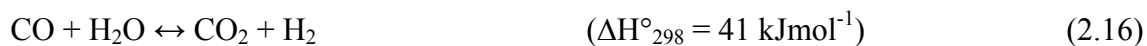
Cracking:



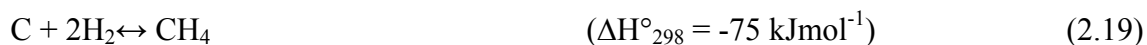
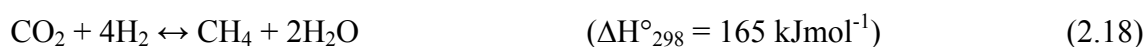
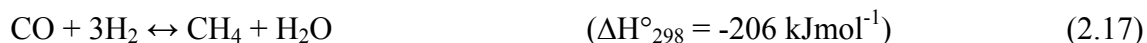
CO₂ reforming:



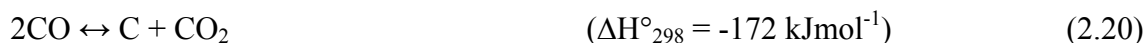
Water-gas shift:



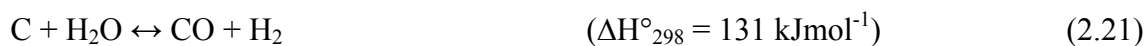
Methanation:



Boudouard:



Carbon gasification:



Thermodynamic calculations based on energy and components balances show that the ATR of isooctane is the most efficient when the O/F ratio is close to unity and the S/F ratio around 2-3. Higher S/F ratios do not improve the hydrogen yield. An optimised reaction composition, in terms of hydrogen production, corresponds to a O/F ratio between 0.5 and 1, and a S/F ratio of 2. Under these conditions, conversion of isooctane is total at 730°C, and the hydrogen level reaches 62% in the reformat. These conditions are close to the calculated thermo neutrality of the reaction.

$$d_n = \frac{H_2 \text{ produced}}{25(C_8H_{18} \text{ reformed} + C_8H_{18} \text{ burnt})} \quad (2.22)$$

$$d_n = \frac{H_2 \text{ produced}}{C_8H_{18} \text{ reformed}}$$

Besides of the research that stated above, there is a lot more research that has been done by using gasoline as their feed. Wang and Zhang (2005), Granovskii et al. (2006). Wang and Wu (2001) have done the research on SR of gasoline for fuel cell applications. Thomas et al. (2000) has compared gasoline, hydrogen, and methanol for fuel options for fuel cell vehicle. Production of hydrogen from gasoline range alkanes with reduced CO₂ emission have been discussed by Otsuka et al. (2002). On-board fuel processor modeling for hydrogen-enriched gasoline fuelled engine has been discussed by Minutillo (2005). Ersoz et al. (2006) compared SREF, POX and ATR systems using using natural gas, gasoline, and diesel as a feed for hydrogen production for PEM fuel cells.

2.3 Steady state simulation of hydrogen production for fuel cell application using gasoline

Reforming options for hydrogen production from fossil fuels (natural gas, gasoline, and diesel) for PEM fuel cells have been discussed by Ersoz et al. (2006). They compared the results of their simulation studies for 100kW PEM fuel cell systems utilizing three different major technologies, namely steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR). The steady state simulation computer code of the Aspen-HYSYS 3.1 process modeling tool has been utilized along with conventional calculation for fuel cell systems. The average molecular weights are around 16.4 kg kmol⁻¹, 94.5 kg kgmol⁻¹ and 215.3 kg kgmol⁻¹ for the natural gas,

gasoline and diesel fuels respectively. The best operation parameters have been determined by change parametrically the S/F, O/F ratios and operation temperatures of reactors. Table 2.4 presents the ranges of operating parameters investigated in the simulation studies.

Table 2.4: The investigated ranges of reformer conditions (Ersoz et al., 2006)

	Temperature (°C)	Pressure (bar)	S/F	O/F
ATR	600-900	3	2.0-3.5	0.25-2.0
PRE-SR	500-550	3	2.0-3.5	-
SR	700-850	3	2.0-3.5	-
POX	800-1100	3	-	0.25-2.0

The simulated PEM fuel cell system consists of the following sections:

- fuel processing section – consists of reforming and clean-up sections (Fig. 2.1)
- PEM fuel cell section
- auxiliary units

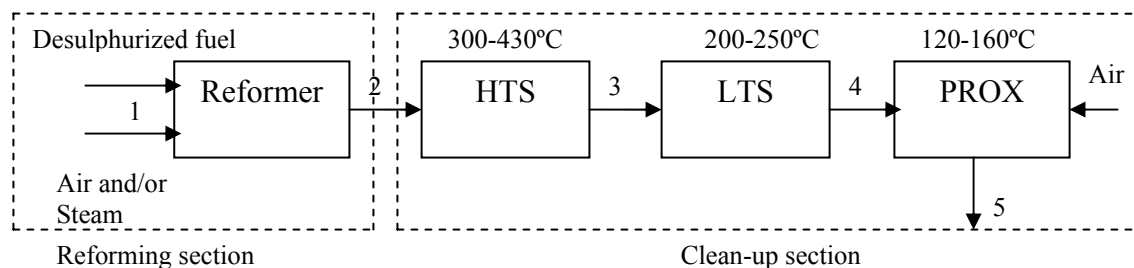


Figure 2.1: Schematic diagram of the fuel reforming and clean-up sections (Ersoz et al., 2006)

The simulation results indicate that the fuel processing efficiencies decrease in order of steam reforming > autothermal reforming > partial oxidation for both gasoline and diesel fuels. Steam reforming appears as the most promising fuel reforming option based on fuel processing efficiencies. The SREF based fuel-processing, fuel cell, auxiliary and overall systems efficiencies of the investigated fuels are presented in table 2.5. The values indicate that natural gas with steam reforming is the best option while there are only minor differences regarding the investigated fuels.

Table 2.5: Steam reforming based fuel processing, fuel cell, auxiliary and overall system efficiency (Ersoz et al., 2006)

Fuel	η_{FP}	η_{FC}	η_{Aux}	$\eta_{net.el}$
Natural gas	98.1	50.6	97.0	48.2
Gasoline	85.5	50.6	95.1	41.1
Diesel	86.3	50.6	97.1	42.4

Previous studies have compared the reforming technologies that are SR, POX and ATR for the hydrogen production using gasoline (Ersoz et al., 2005). The comparison is based on the efficiencies of the overall fuel cell systems with the selected fuel reforming options. The Aspen HYSYS 3.1 code has been used for simulation purposes.

Doss et al. (2001) does a parametric analysis on fuel processors for automotive fuel cell systems. The analyses have been conducted using GCtool, a software package developed at Argonne National Laboratory in the steady state operation. They had identified the influence of various operating parameters on the system performance such as operating pressure (3 and 1 atm), reforming temperature (1000-1300K), steam-to-fuel and air-to-fuel reactant feed ratios, electrochemical fuel utilization, and thermal integration of the fuel processor and the fuel cell stack subsystems. From the analyses, at

the thermodynamic equilibrium, it was determined that reforming temperatures of 1100K, a water-to-carbon mole ratio of 1.5-2.5, and the use of fuel cell exhaust energy in the fuel processor subsystem can yield fuel processor efficiencies of 82-84%, and total system efficiencies of 40-42% can be achieved.

Hamid et al. (2006) have done a simulation of catalytic autothermal reforming (ATR) of methane (CH_4) for hydrogen (H_2) production. A model is developed using HYSYS 2004.1 to simulate the conversion behavior of the reformer. Figure 2.2 presents the principle of a scheme of an ATR process. The model covers all aspects of major chemical kinetics and heat and mass transfer phenomena in the reformer. The ATR and preferential oxidation (PROX) processes is modeled using conversion reactor, while the water gas shift (WGS) process is modeled using equilibrium reactor within HYSYS environment.

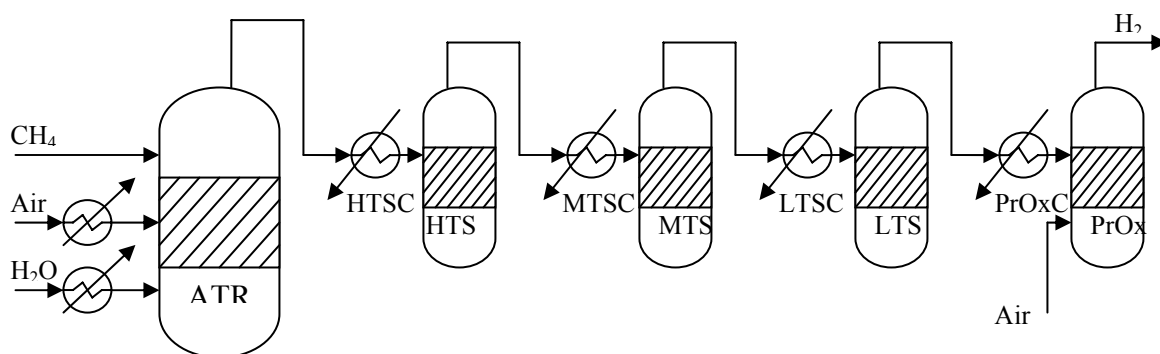


Figure 2.2: Principle of a scheme of an ATR process (Hamid et al., 2006)

There is also a previous study on simulation of PEM fuel cell system with auto thermal reforming. This research has been done by Ersoz et al., (2003). The operation condition has studied in detail to determine the values, which lead to the production of a hydrogen rich gas mixture with CO concentration remain below 10 ppm under steady state operation.

2.4 Summary

There are a lot of research that had been carried out to produce hydrogen from gasoline via different methods such as SREF, POX and ATR. From the literature study, the hydrogen production from ATR seem to be the most promising concept for mobile applications because the reactor design is much simpler (smaller and lighter unit), than that of conventional steam reformer with internal heat exchanger. Besides of that, it also offers advantages of lower operating temperature, flexible load following characteristics as compared to the SREF process and has higher energy efficiency than the POX process. The ATR of n-octane involves a complex set of chemical reactions such as total oxidation, partial oxidation, steam reforming, methanation, CO₂ reforming, cracking, boudouard and carbon gasification.

CHAPTER III

METHODOLOGY

3.1 Research Tools

This research was carried out using Aspen HYSYS 2004.1 simulator for process flowsheeting to provide data regional analyses. Aspen HYSYS 2004.1 simulator was used to perform the new process model control structure for hydrogen production using gasoline as a raw material for fuel cell application.

3.1.1 Aspen HYSYS 2004.1

Aspen HYSYS 2004.1 was a product of AEA Technology, which is now part of Aspentech Engineering Suite (AES). Aspen HYSYS 2004.1 has been chosen as the

process simulator for this research because of two main advantages over the other software packages. It can interactively interpret commands as they are entered one at a time. Others require execution after new entries. Aspen HYSYS 2004.1 has the unique feature that information propagates both in forward and reverse directions, performing back-calculations in a non-sequential manner. The bi-directionality often makes iterative calculations unnecessary and the solution is fast.

3.2 Research Activities

There are several activities that had been done to achieve the objective of this research which are to simulate and optimize the n-octane autothermal reformer for hydrogen production for fuel cell applications.

3.2.1 Data Collection

General understanding of the process has to be obtained at this stage. The physical properties of the gasoline type hydrocarbon fuel (n-octane) used in the simulation studies is given in Table 3.1. The average molecular weight is around 94.5 kg/kmol. The fuel is assumed to be sulphur free. Hence, there is no need for any desulphurization process within the frame of this study.

Table 3.1: Physical properties of n-octane

Formula	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
Form	Liquid
Colour	Clear, colourless
Boiling point/range	122-124°C
Odour Characteristic	Mild
Melting point/range	-56.5°C
Flash point	12°C
Autoignition temperature	210°C

The best operations parameters have been determined by change parametrically the O/C ratios and operation temperatures of reactors. Table 3.2 presents the ranges of operating parameters investigated in the simulation studies.

Table 3.2: The investigated ranges of ATR conditions (Ersoz et al., 2006)

	Temperature (°C)	Pressure (bar)	O/C
ATR	600-900	3	0.25-2.0

3.2.2 Steady State Model Development

The design and optimization of a chemical process involve the study steady state behavior. Steady state models can perform steady state energy and material balances and evaluate different plant scenarios. The design engineer can use steady state simulation to optimize the process by reducing capital and equipment costs while maximizing production.

The integrated steady state modeling capabilities, where the same model can be evaluated from either perspective with full sharing of process information, represents a significant advancement in the industry. The use of chemical flow sheeting software has become an integral part of the evaluation of the performance of the fuel cell systems. The process simulation package Aspen HYSYS 2004.1 has been used along with conventional calculations in this study.

3.2.3 Steady State Model Validation

At this stage, the output from the simulation above was compared with the calculated results from mathematical analysis based on the stoichiometry of the overall reaction. Data generation according to certain characteristic as desired by state space modeling technique will be carried out using simulator.

3.2.4 ATR Optimization

The primary operating variables in autothermal reforming are the S/F and A/F ratios. These two ratios, along with the degree of preheat of the fuel, air and water (or steam) determines the reaction temperature in the reformer (referred to as the ATR Vap T). Different combination of the S/F and A/F ratios may yield the desired ATR Vap T; however, with the same ATR Vap T but with different feed conditions, the reformate gas composition can be different, in turn yielding different fuel processor and system efficiencies.

3.2.5 Heat Integration

The other major components of the fuel processing subsystem are the various heat exchanger, boilers and coolers used for preheating the process streams and heat recovery between the different process steps. This thermal integration is essential for achieving a high efficiency in the fuel processor and in the entire fuel cell power system.

3.2.6 CO Clean up

PEMFC possess a series of advantageous features that make them leading candidates for mobile vehicle power applications or small stationary power units, low

operating temperature, sustained operation at high current density, low weight, as well as suitability to discontinuous operation, etc (Wang and Zhang, 2005). However, the ideal fuel for PEMFC is pure hydrogen, with less than 10 ppm carbon monoxide, as dictated by the poisoning limit of the Pt fuel cell catalyst. Therefore, CO clean up section is crucial for the fuel processing. Water-gas shift (WGS) reaction is one of the methods to reduce the concentration of CO. WGS section consists of high-temperature shift (HTS), medium-temperature shift (MTS) and high-temperature shift (HTS) reactor. However, even after the WGS reaction, small amounts of CO still exist. So, preferential oxidation (PROX) appeared to be the preferred solution. In the PROX reaction system, CO and hydrogen will be converting to CO₂ and water with the existing of air.

3.2.7 Plant wide optimization

As previously stated, the A/F and S/F ratio is a critical parameter for ATR. For this section, the influence of the S/F ratio and the amount of air that will be injected to PROX to the fuel processor performance is investigated. Plant wide optimization process is very important in order to determine the optimum operating conditions and parameters to achieve high production of hydrogen and at the same time low CO concentration.

3.3 Summary

All of the steps of the research methodology that had been discussed at the previous section are important in order to achieve the optimum production of hydrogen with low carbon monoxide concentration. Figure below shows the flowchart of the methodology that had been carried out in this research.

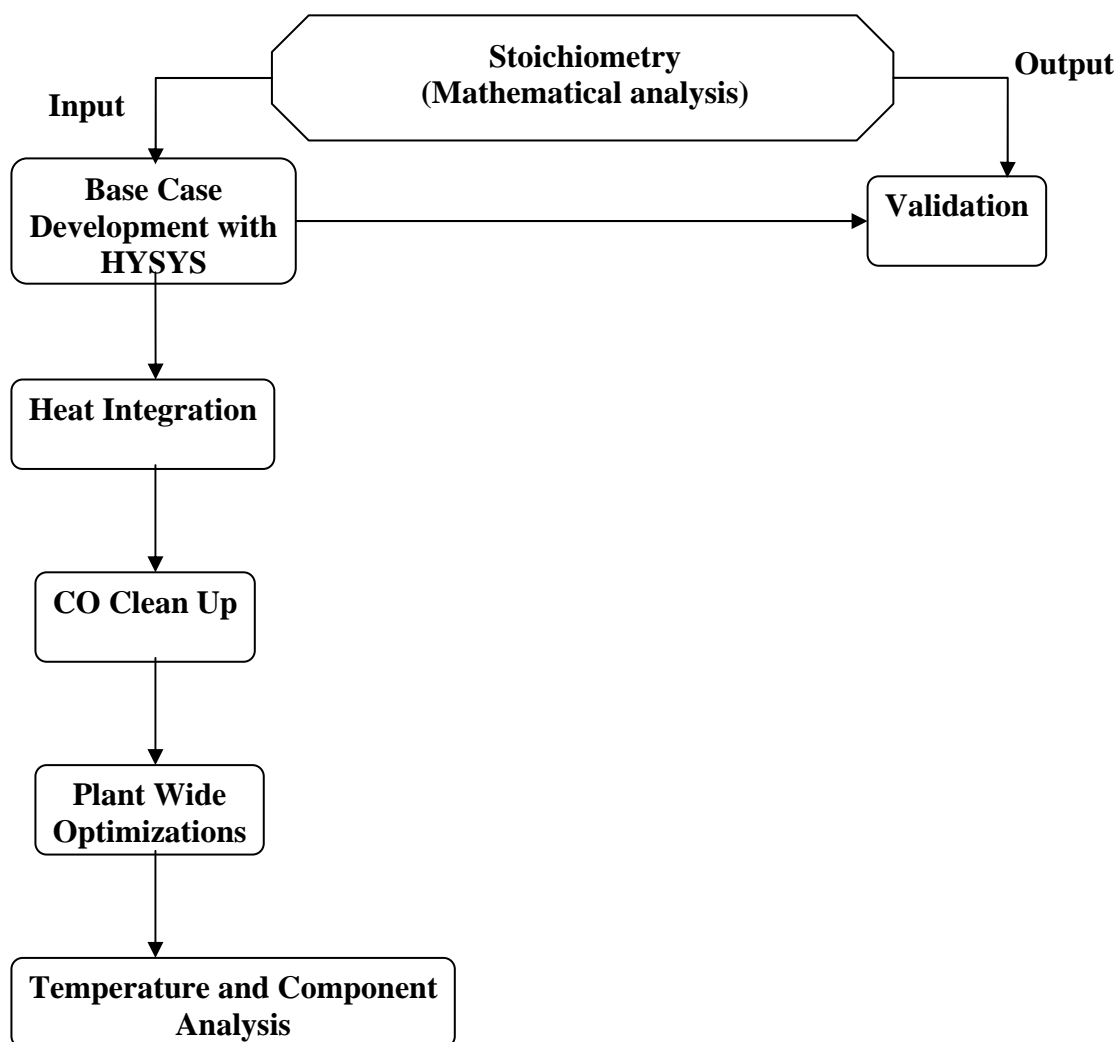


Figure 3.1: Flowchart of the methodology

CHAPTER IV

STEADY STATE SIMULATION OF HYDROGEN PRODUCTION FOR FUEL CELL APPLICATION

4.1 Process Description of Hydrogen Production for Fuel Cell Application

In this case study, the PEM fuel cell system consists of the fuel processing and clean-up section, PEM fuel cell section and auxiliary units. Figure 4.1 present a simplified schematic of the fuel processing and clean –up section.

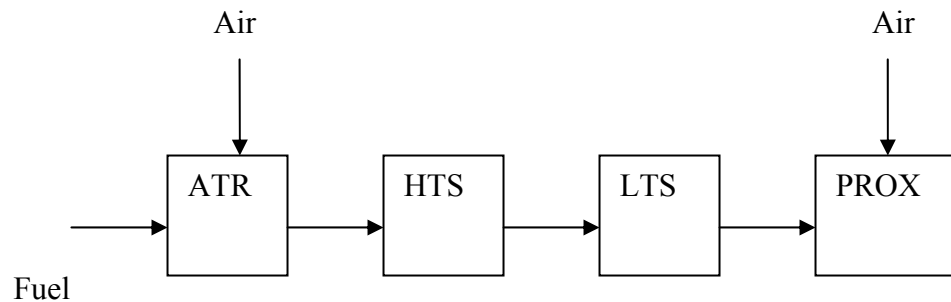


Figure 4.1: A schematic diagram of the fuel processing and clean –up section

(Ersoz et al., 2006)

Part of the gasoline type hydrocarbon fuel and air are first fed to the ATR reactor. Here, the hydrogen is produced under adiabatic conditions. The other portion of the fuel is utilized in the combustor, which provides process heat for various fuel cell system components. It is desired to maximize hydrogen concentration and to minimize carbon monoxide content considering the requirements of PEM fuel cells.

The high and low temperature water-gas shift reactors (HTS and LTS) are used to decrease the CO concentration level of the ATR reactor exit gas to the desired values. The last step is preferential oxidation (PROX) to convert the left over CO to CO₂. ATR, HTS, LTS, and PROX reactors are simulated as adiabatic systems.

4.2 Modelling and Simulation of Hydrogen Production for Fuel Cell Application

The fuel cell plant is simulated using Aspen HYSYS 2004.1 software. Typically the simulation process takes the following stages:

- (i) Preparation Stage
 - (a) Selecting the thermodynamic model
 - (b) Defining chemical components

- (ii) Building Stage
 - (a) Adding and defining streams
 - (b) Adding and defining unit operations
 - (c) Connecting streams to unit operations
 - (d) Installing valves and controllers

- (iii) Execution stages
(a) Starting integration

Aspen HYSYS 2004.1 is made up of four major parts to form rigorous modelling and simulation environment.

- A component library consisting of pure component physical properties
- Thermodynamic packages for transport and physical properties prediction
- Integrator for dynamic simulation and/or solver for steady-state simulation
- Mathematical modelling of unit operation

This is demonstrated in Figure 4.1. For this study, each of the above components is described in section below.

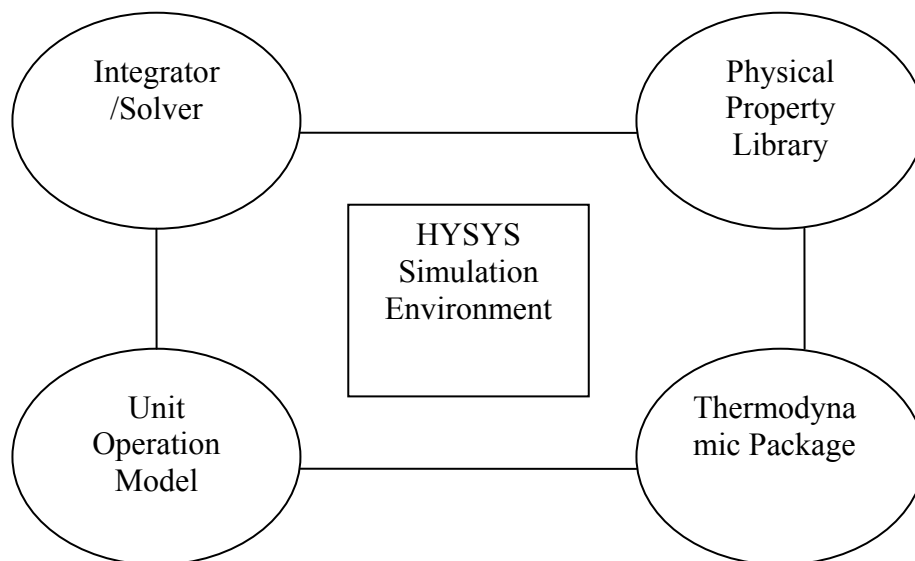


Figure 4.2: HYSYS simulation environment

4.2.1 Physical Properties of the Pure Component

Part of the gasoline type hydrocarbon fuel is the feedstock to the process. This fuel consists of numerous components, and is obtained by processing crude oil in petroleum refinery. For this study, we used n-octane to represent the gasoline fuel. Table 4.1 shows the physical properties of n-octane.

Table 4.1: The physical properties of n-octane

Formula	$\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
Form	Liquid
Colour	Clear, colourless
Boiling point/range	122-124°C
Odour Characteristic	Mild
Melting point/range	-56.5°C
Flash point	12°C
Autoignition temperature	210°C

4.2.2 Thermodynamic Property

In physics and thermodynamics, an equation of state is a constitutive equation describing the state of matter under a given set of physical conditions. It provides a mathematical relationship between two or more state functions associated with the matter, such as its temperature, pressure, volume, or internal energy. Equations of state are useful in describing the properties of fluids, mixtures of fluids, solids, and even the interior of stars. The most prominent use of an equation of state is to predict the state of gases and liquids.

The Peng-Robinson Equation of State (EoS) is the EoS most widely used in chemical engineering thermodynamics. It is enhanced by Hyprotech for its wider applicability. It is known to give slightly better predictions of liquid densities than the Soave-Redlich-Kwong EOS by Soave (1972). The EOS requires three inputs per compound: T_c , P_c and the acentric factor ω .

The Peng-Robinson equation of state

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2} \quad (4.1)$$

R = ideal gas constant (8.31451 J/ (mol K))

$$a = \frac{0.45724R^2T_c^2}{P_c} \quad (4.2)$$

$$b = \frac{0.07780RT_c}{P_c} \quad (4.3)$$

$$\alpha = (1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) (1 - T_r^{0.5}))^2 \quad (4.4)$$

$$T_r = \frac{T}{T_c} \quad (4.5)$$

The Peng-Robinson equation was developed in 1976 in order to satisfy the following goals:

1. The parameters should be expressible in terms of the critical properties and the acentric factor.
2. The model should provide reasonable accuracy near the critical point, particularly for calculations of the Compressibility factor and liquid density.
3. The mixing rules should not employ more than a single binary interaction parameter, which should be independent of temperature pressure and composition.
4. The equation should be applicable to all calculations of all fluid properties in natural gas processes.

For the most part the Peng-Robinson equation exhibits performance similar to the Soave equation, although it is generally superior in predicting the liquid densities of many materials, especially nonpolar ones.

4.2.3 Integration Algorithm

A dynamic model is represented by a set of ordinary differential equations (ODEs) in Aspen HYSYS 2004.1. In order to solve the model, an implicit Euler method

is used to integrate the ODEs. The fixed step size implicit Euler method explained here is also known as the rectangular integration. It can be described by extending a line of slope zero and length h (the step size) from t_n to t_{n+1} on a $f(Y)$ versus time plot. The area under the curve is approximated by a rectangle of length h and height $f_{n+1}(Y_{n+1})$ in a function of the following form (HYSYS Documentation, 2000).

$$Y_{n+1} = Y_n + \int_{t_n}^{t_{n+1}} f(Y) dt, \text{ where: } \frac{dY}{dt} = f(Y) \quad (4.6)$$

To provide a balance between accuracy and speed, Aspen HYSYS 2004.1 employs a unique integration strategy. The volume, energy, and 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 2004.1 to increase the speed or stability of the system. The default value of 0.5 second was selected.

4.2.4 Mathematical Modelling of the Reactor Operation

4.2.4.1 Linear and Non-Linear Systems

A linear first-order Ordinary Differential Equation (ODE) can be described as follows:

$$\tau \frac{dY}{dt} + Y = Kf(u) \quad (4.7)$$

In a non-linear equation, the process variable Y may appear as a power, exponential, or is not independent of other process variables. Here are two examples:

$$\tau \frac{dY}{dT} + Y^3 = Kf(u) \quad (4.8)$$

$$\tau \frac{dY}{dt} + YY_2 = Kf(u) \quad (4.9)$$

The great majority of chemical engineering processes occurring in nature are nonlinear. Nonlinearity may arise from equations describing equilibrium behavior, fluid flow behavior, or reaction rates of chemical systems. While a linear system of equations may be solved analytically using matrix algebra, the solution to a non-linear set of equations usually requires the aid of a computer.

4.2.4.2 Material Balance

The conservation relationships are the basis of mathematical modeling in HYSYS. The dynamic mass, component, and energy balances that are derived in the following section are similar to the steady-state balances with the exception of the accumulation term in the dynamic balance. It is the accumulation term which allows the output variables from the system to vary with time. The conservation of mass is maintained in the following general relation:

Rate of accumulation of mass = mass flow into system - mass flow out of system

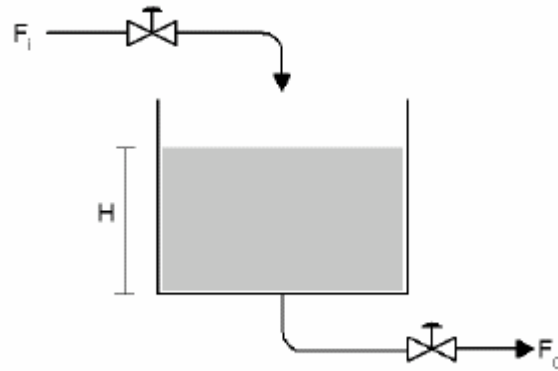


Figure 4.3: Reactor Operating

$$d \frac{d(\rho_o V)}{dt} = F_i \rho_i - F_o \rho_o \quad (4.10)$$

Where:

F_i = the flow rate of the feed entering the reactor tank

ρ_i = the density of the feed entering the reactor tank

F_o = the flow rate of the product exiting the reactor tank

ρ_o = the density of the product exiting the reactor tank

V = the volume of the fluid in the reactor tank

4.2.4.3 Component Balance

Component balances can be written as follows:

Rate of accumulation of component j =
Flow of component j into system
- Flow of component j out of system
+ Rate of formation of component j by reaction

Flow into or out of the system can be convective (bulk flow) and/or molecular (diffusion). While convective flow contributes to the majority of the flow into and out of a system, diffusive flow may be significant if there is a high interfacial area to volume ratio for a particular phase. For a multi-component feed for a perfectly mixed tank, the balance for component j would be as follows:

$$\frac{d(C_{jo}V)}{dt} = F_i C_{ji} - F_o C_{jo} + R_j V \quad (4.11)$$

Where:

C_{ji} = the concentration of j in the inlet stream

C_{jo} = the concentration of j in the outlet stream

R_j = the reaction of rate of the generation of component j

For a system with NC components, there are NC component balances. The total mass balance and component balances are not independent; in general, you would write the mass balance and $NC-1$ component balances.

4.2.4.4 Energy Balance

The Energy balance is as follows:

Rate of accumulation of total energy =
Flow of total energy into system - Flow of total energy out of system
 + *Heat added to system across its boundary*
 + *Heat generated by reaction*
 - *Work done by system on surroundings*

The flow of energy into or out of the system is by convection or conduction. Heat added to the system across its boundary is by conduction or radiation. For a CSTR with heat removal, the following general equation applies:

$$\frac{d}{dt}[(u + k + \phi)V] = F_i \rho_i (u_i + k_i \phi_i) - F_o \rho_o (u_o + k_o + \phi_o) + Q + Q_r - (w + F_o P_o - F_i P_i) \quad (4.12)$$

Where:

u = Internal energy (energy per unit mass)

k = Kinetic energy (energy per unit mass)

f = Potential energy (energy per unit mass)

V = the volume of the fluid

w = Shaft work done by system (energy per time)

P_o = Vessel pressure

P_i = Pressure of feed stream

Q = Heat added across boundary

Q_r = Heat generated by reaction: DH_rxn_rA

Several simplifying assumptions can usually be made: The potential energy can almost always be ignored; the inlet and outlet elevations are roughly equal. The inlet and outlet velocities are not high, therefore kinetic energy terms are negligible. • If there is no shaft work (no pump), $w=0$.

The general energy balance for a 2-phase system is as follows:

$$\frac{d}{dt}[\rho_v V_v H + \rho_l V_l h] = F_i \rho_i h_i - F_l \rho_l h - F_v \rho_v H + Q + Q_r \quad (4.13)$$

4.2.5 Pump Model

Pumps were used to increase the pressure of inlet liquid streams by providing energy in the form of shaft work to the system. A pump operation in Aspen HYSYS 2004.1 assumes that the inlet fluid is incompressible. Therefore, the operation of the pump is calculated in terms of the ideal power, W :

$$W = \frac{(P2 - P1)F(MW)}{p} \quad (4.14)$$

Here $P1$ denotes the pressure of the inlet stream, $P2$ the pressure of the exit stream, ρ the density of the inlet stream, F the molar flowrate of the stream of the stream and MW the molecular weight of the fluid.

4.2.6 Mixer, Splitter (Tee) and Valve Models

The mixer combines two or more inlet streams to produce an outlet stream. There are two possible dynamic specifications concerning the pressures of the surrounding streams to choose to characterize the mixer operation. They are “Equalize All” and “Set Outlet to Lowest Inlet”. The first specification equalizes the pressure of the inlet streams and was selected because in an actual plant, the inlet stream pressures to a mixer must be the same.

The tee splits one feed stream into multiple product streams. In the simulation, the split fractions of the exit streams are determined automatically from the pressure network. The new valve operation model in this version of Aspen HYSYS 2004.1 controls the valve much more realistically. The direction of flow through a valve is dependent on the pressures of the surrounding unit operations. A fluid flowing through a valve is calculated from the frictional pressure loss of the valve and the pressure loss from static head contributions. This calculation allows the modelling of flow reversal situation.

4.2.7 Compressor

Gas compressor (including fans and blowers) unlike pumps, are designed to increase the velocity and/or pressure of gases rather than liquids. In fact, small amounts of liquid can cause significant amounts of degradation to the compressor blades, and consequently, most compressor systems are designed to prevent liquid from entering the compressor and to avoid condensation in the compressor. The main methods used to

move gas are centrifugal force, displacement, and transfer of momentum. The isentropic efficiency of the compressor is defined as:

$$\eta_s = \frac{\dot{W}_{isentropic}}{\dot{W}_{brake}} = \frac{h_{2,isentropic} - h_1}{h_2 - h_1} \quad (4.15)$$

4.2.8 Expander

Expanders (also called turbo expanders and expansion turbines) are often used, in place of valves, to recover power from a gas when its pressure must be decreased. At the same time, the temperature of the gas is reduced and often the chilling of the gas is more important than the power recovery. The effect of the expander efficiency is just the opposite of the compressor efficiency, which is:

$$\eta_s = \frac{\dot{W}_{brake}}{\dot{W}_{isentropic}} = \frac{h_1 - h_2}{h_1 - h_{2,isentropic}} \quad (4.16)$$

4.2.9 Furnaces

Furnaces (also called fired heaters) are often to heat, vaporize, and/or react process streams at high temperatures and high flow rates. Heat duties of commercial units are in the range of 3 to 100 MW (10,000,000 to 340,000,000 Btu/hr). A number of

different designs exist, using either rectangular or cylindrical steel chambers, lined with firebrick.

4.2.10 Cooler/Heater Model

In Aspen HYSYS 2004.1, a cooler (or heater) operation can be specified either by choosing the direct duty option or the utility fluid option. It was fully understood that the accuracy of the simulation would be

4.2.11 Degree of Freedom Analysis

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. There are two type of degree of freedom. The first one is dynamic degrees of freedom, N_m (here m denotes manipulated). N_m is usually easily obtained by process insight as the number of the 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. Next, 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_m .

- N_{om} is the number of manipulated (input) variables with no steady-state effect (or more generally, with no effect on the operation cost). Typically, these are extra

manipulated variables used to improve the dynamic response, e.g. an extra bypass on a heat exchanger.

- N_{oy} is the number of (output) variables that need to be controlled, but which has no steady-state effect (or more generally, no effect on the operation cost). Typically, these are liquid levels in holdup tanks.

As a result, Equation 4.6 is obtained.

$$N_{ss} = N_m - (N_{om} + N_{oy}) \quad (4.13)$$

4.2.12 Steady State Simulation

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 (HYSYS Manual, 2000).

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. The result obtained from steady state simulation was used as the initial condition for the dynamic simulation.

4.3 Summary

For the steady state simulation of hydrogen production plant, there are several stages that involved which are preparation stages, building stages and execution stage.

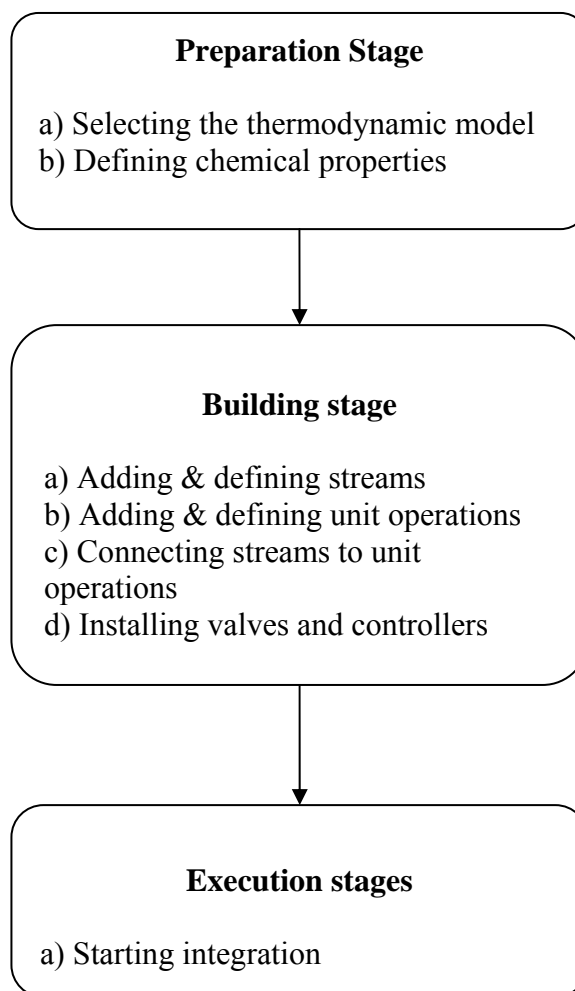


Figure 4.4: Stages in the simulation process

CHAPTER V

RESULTS AND DISCUSSION

5.1 Base case development

The PEM fuel cell system consists of fuel processing section, PEM fuel cell section and auxiliary units. Fuel processing consists of reforming and clean up sections. The reforming section contains the reforming reactor which is an autothermal reactor (ATR). Figure 5.1 shows the process flow diagram of an ATR which has been building using ASPEN Hysys 2004.1. The feed streams of air, water and gasoline are heated up from 25°C to approximately 150°C in the heater. After that, the feed streams are directed to the ATR, where gasoline is converted autothermally.

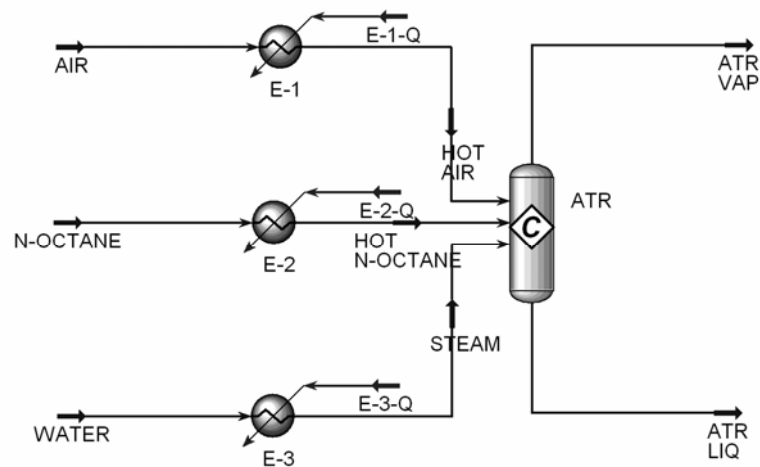
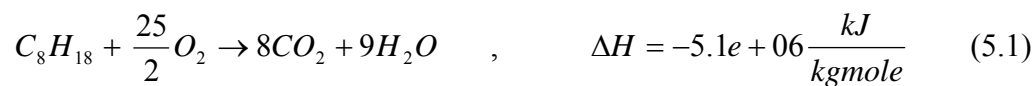


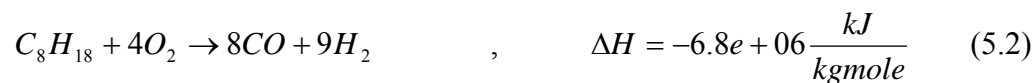
Figure 5.1: Process flow diagram of ATR

The combined reforming of n-octane involves a complex set of chemical reactions, in which primary reactions lead to decomposition of hydrocarbons such as POX, TOX, and SR. POX and TOX do not require indirect heating in contrast to steam reforming. POX is known as the conversion of hydrocarbons with substoichiometric supply of oxygen. Depending on the oxygen ratio λ which $\lambda = 1$ corresponds to complete combustion to carbon dioxide and steam (Springmann et al., 2002). POX of hydrocarbons can be thermally neutral to strongly exothermic. Partial oxidation needs external cooling and generates a high concentration of CO, which is not desired for fuel cell applications.

Total oxidation

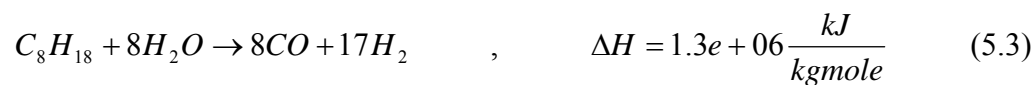


Partial oxidation

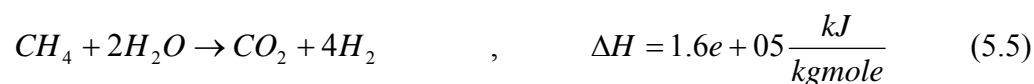
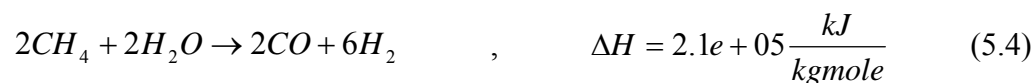


SR is an endothermic process leading to hydrogen, carbon monoxide and carbon dioxide and is catalyzed by nickel or noble metal catalysts (Springmann et al. 2002). Steam reforming is one of the least expensive hydrogen production methods (Wang and Zhang, 2005). Furthermore, it is able to produce high hydrogen concentration in the reformed gas, about 70%. Therefore the efficiency of hydrogen production is high.

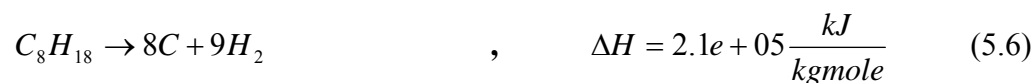
Steam reforming



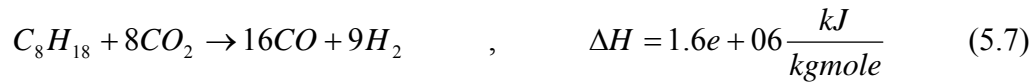
Steam reforming Methane



Cracking

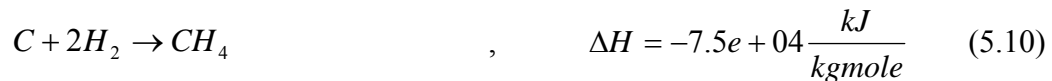
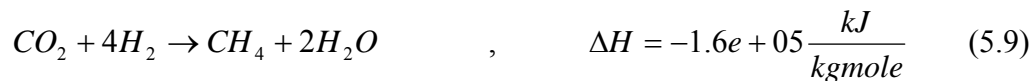
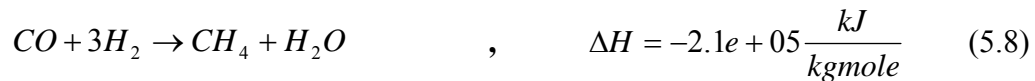


CO₂ Reforming

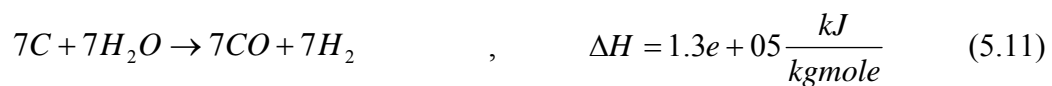


There are also many secondary reactions take place between the different products together and with steam.

Methanation

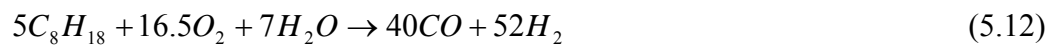


Carbon Gasification



However, because of the parallel reactions above, the stoichiometry of n-octane ATR is best described as:

Overall Reaction



From the overall reaction, we can get the stoichiometry of n-octane ATR and from this stoichiometry we can calculate the component molar flow of input and output.

Basis for calculation:

$$100 \frac{\text{kmol}}{\text{h}} C_8H_{18}$$

Table 5.1: Component molar flow of the input and output stream of the ATR

Comp Molar Flow (kg mole/h)	Input	Output
n-octane	100.00	0.00
Water	140.00	0.00
Oxygen	330.00	0.00
Nitrogen	1241.43	0.00
Carbon monoxide	-	800.00
Hydrogen	-	1040.00
Carbon	-	0.00
Methane	-	0.00
Carbon dioxide	-	0.00

5.2 Base case validation

At this stage, the data that had been calculated based on ATR stoichiometry was insert to the simulator. The simulator that had been used in this study is Aspen Hysys 2004.1. The results from this simulation were compared with the calculated data as stated before. Table below shows the results from the simulation process.

Table 5.2: Simulation results of the ATR using Aspen Hysys 2004.1

Name	HOT AIR	HOT ISO OCTANE	STEAM	ATR VAP
Vapour fraction	1.00	1.00	1.00	1.00
Temperature	150.00	150.00	150.00	492.43
Pressure	101.32	101.32	101.32	101.32
Molar flow (kgmole/h)	1571.43	100.00	140.00	3081.43
Comp Molar Flow (n-octane) (kgmole/h)	0.00	100.00	0.00	0.00
Comp Molar Flow (CO) (kgmole/h)	0.00	0.00	0.00	800.00
Comp Molar Flow (Hydrogen) (kgmole/h)	0.00	0.00	0.00	1040.00
Comp Molar Flow (CO ₂) (kgmole/h)	0.00	0.00	0.00	0.00
Comp Molar Flow (Oxygen) (kgmole/h)	330.00	0.00	0.00	0.00
Comp Molar Flow (Nitrogen) (kgmole/h)	1241.43	0.00	0.00	1241.43
Comp Molar Flow (H ₂ O) (kgmole/h)	0.00	0.00	140.00	0.00
Comp Molar Flow (Carbon) (kgmole/h)	0.00	0.00	0.00	0.00
Comp Molar Flow (Methane) (kgmole/h)	0.00	0.00	0.00	0.00

From the results of this simulation, we can calculate the error between the calculated and simulated data. The error can be calculated by using this formula:

$$Error(\%) = \frac{\text{simulated} - \text{calculated}}{\text{calculated}} \times 100$$

Table 5.3: Error percentage between the calculated and simulated data

	Input			Output		
	Calculated	Simulated	Error (%)	Calculated	Simulated	Error (%)
Comp Molar Flow (n-octane) (kgmole/h)	100.00	100.00	0.00	0.00	0.00	0.00
Comp Molar Flow (CO) (kgmole/h)	0.00	0.00	0.00	800.00	800.00	0.00
Comp Molar Flow (Hydrogen) (kgmole/h)	0.00	0.00	0.00	1040.00	1040.00	0.00
Comp Molar Flow (CO ₂) (kgmole/h)	0.00	0.00	0.00	0.00	0.00	0.00
Comp Molar Flow (Oxygen) (kgmole/h)	330.00	330.00	0.00	0.00	0.00	0.00
Comp Molar Flow (Nitrogen) (kgmole/h)	1241.43	1241.43	0.00	1241.43	1241.43	0.00
Comp Molar Flow (H ₂ O) (kgmole/h)	140.00	140.00	0.00	0.00	0.00	0.00
Comp Molar Flow (Carbon) (kgmole/h)	0.00	0.00	0.00	0.00	0.00	0.00
Comp Molar Flow (Methane) (kgmole/h)	0.00	0.00	0.00	0.00	0.00	0.00

From the error that had been calculated, we can conclude that the base case simulation is valid and can be used as a real plant for further analysis. This is because there is no error between the calculated and simulated results using Aspen Hysys 2004.1.

5.3 ATR optimization

The process of converting gasoline to fuel gas suitable for feeding to the anode of the fuel cell stack consists of several steps. First, the n-octane is reacted with air and water in the ATR to form a gas mixture of H_2 , CO , N_2 , H_2O and CH_4 . ATR optimization process is important in order to determine the optimum operating conditions for ATR. The primary operating variables in autothermal reforming are the air-to-fuel and steam-to-fuel ratios. These two ratios, along with the degree of preheat of the fuel, air, and water (or steam) determines the reaction temperature in the reformer (referred to as the ATR Vap T in the present analyses).

In order to determine the optimum value of air molar flow inlet, the values were varied from 1000 to 2000, whereas water molar flow was set at the calculated value and n-octane molar flow at 100 kgmole/h. The desired ATR Vap T for this analysis is approximately $700^\circ C$ or higher. This range of temperature was selected because at these temperatures, most of the carbon in the fuel is converted to CO or CO_2 . From the graph, at Figure 5.2, we can see that the hydrogen production is constant at 1040 kgmole/h when air molar flow is increasing from 1000 to 1550 kgmole/h while CO molar flow increased proportionally with air molar flow and become constant at 800 kgmole/h after 1600 kgmole/h of air. In spite of this, the temperature of the outlet ATR is below $700^\circ C$ in this region, so there is no optimum value at this area.

At too high air molar flow (or can be call as A/F ratio), however, the combustion of n-octane becomes detrimental to the hydrogen production. Though, the ATR outlet temperature is above $700^\circ C$ at this region, so the optimum value of air molar flow is 1850 kgmole/h. The ATR outlet temperature has to be more than $700^\circ C$ because we need a lot of heat to do the heat integration. Table 5.4 shows the results of the conditions and compositions of ATR effluent and feed stream before and after optimization.

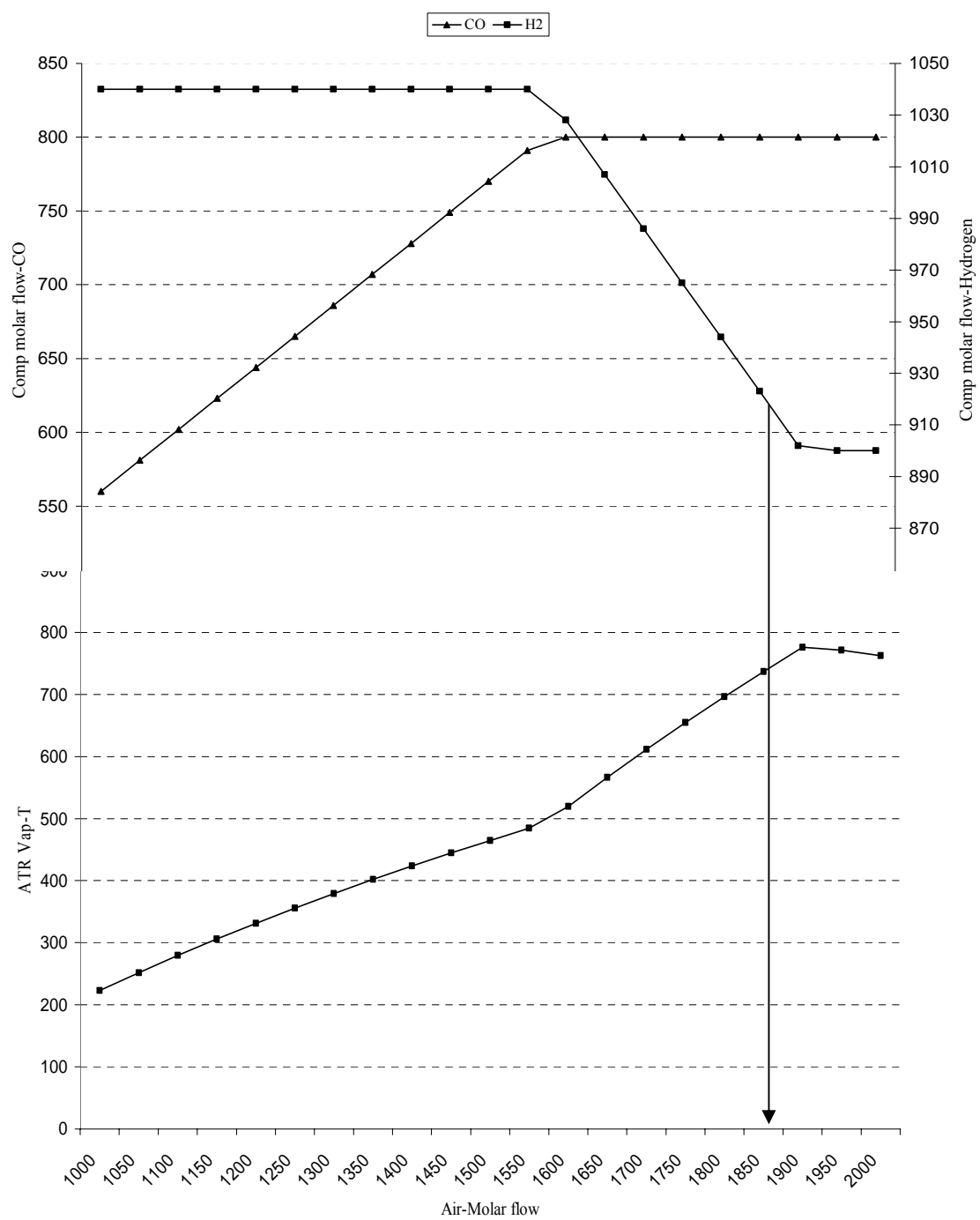


Figure 5.2: Influence of the air molar flow on the hydrogen, CO composition and ATR outlet temperature

5.4 Heat integration

The other major components of the fuel processing subsystem are the various heat exchanger, boilers and coolers used for preheating the process streams and heat recovery between the different process steps. This thermal integration is essential for achieving a high efficiency in the fuel processor and in the entire fuel cell power system. For instance, the degrees of air preheat and steam superheat for the feeds to the ATR reactor can affect the fuel processing efficiencies significantly.

In this study, tube and shell type heat exchanger with co current flow is used. Figure 5.3 shows the process flow diagram of the heat integration in this study. A device used to transfer heat from a fluid flowing on one side of a barrier to another fluid (or fluids) flowing on the other side of the barrier. For the first heat exchanger (EX-1), the fluid of ATR Vap stream enters the heat exchanger at shell side with temperature of 736.7°C , while at the tube side n-octane enters the heat exchanger with temperature of 25°C . The desired outlet temperature of the fluid at the tube side is 150°C . Then, the outlet fluid at shell side from EX-1 (ex-2 in), enters the second heat exchanger with temperature of 672.9°C .

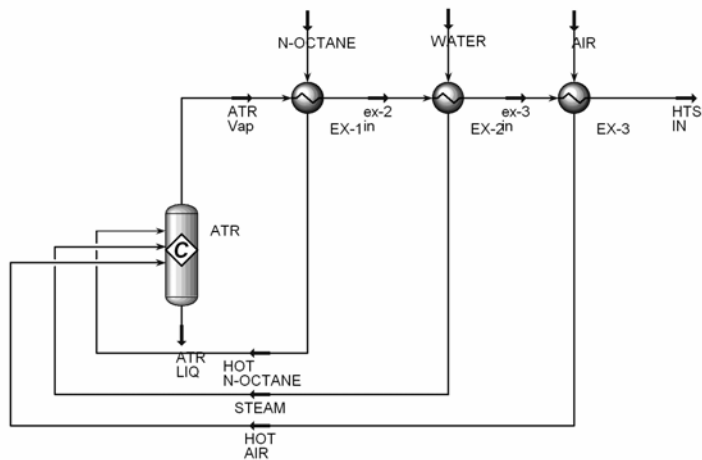


Figure 5.3: Process flow diagram of heat integration

At the same time, water enters the tube side with temperature of 25°C , and the heat transfer process happen and brings up the water temperature to 150°C , while the temperature of outlet fluid from shell side decreases to 608.6°C . So, at this moment water become steam. The same process happen at third heat exchanger (EX-3), the temperature of the fluid enters the shell side is 608.6°C , as for the tube side, air flows with temperature of 25°C . After heat transfer process occurred, the outlet temperature of fluid at the shell side is decreased to 543.3°C and the air temperature increases to 150°C . The temperature profile of the heat integration that been discussed above shown in Figure 5.4.



Figure 5.4: Temperature profile of the heat integration

5.5 CO clean up section

The reformed fuel often contains other gases such as carbon monoxide that are detrimental to PEMFC operation. The carbon monoxide contained in the reformat must be further reduced to 10 ppm prior to feeding to the PEM fuel cell. Various options for carbon monoxide reduction include water-gas shift (WGS), preferential oxidation (PROX) of carbon monoxide, methanation, membrane separators and combinations of these reforming reactor. In this study, WGS and PROX reaction were selected as the reaction for carbon monoxide clean up section.

5.5.1 Water-gas shift (WGS)

From the process flow diagram in Figure 5.5 below, this water-gas shift reaction is carried out in three stages. The high-temperature shift reactor (HTS) is used to convert part of the carbon monoxide, followed by medium-temperature shift (MTS) and low-temperature shift (LTS) to provide further reduction in the concentration of carbon monoxide in the reformat. The water gas shift reaction is an inorganic chemical reaction in which water and carbon monoxide react to form carbon dioxide and hydrogen (water splitting).

Water-gas shift



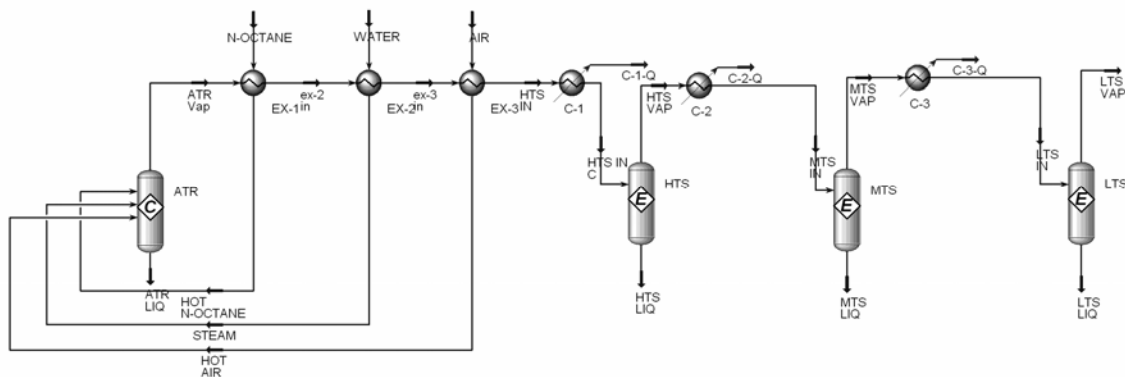


Figure 5.5: Process flow diagram of WGS

For the analysis discussed here, the inlet temperature for HTS is set at 100°C while MTS and LTS are set at 55°C . At these shift reactor temperature, the carbon monoxide concentration at the exit from LTS is typically less than 1% by volume. However, as stated at Eq. 5.13, this reaction needs water (or steam) to convert carbon monoxide to carbon dioxide. From table 5.5, the amount of steam at inlet stream of HTS is 117 kgmole/h while carbon monoxide is 800 kgmole/h. After entering HTS, the amount of carbon monoxide is decrease to 683.21 kgmole/h, and steam also decrease to 0.21 kgmole/h. With a very little amount of steam, there were no water gas shift reaction occur at HTS and MTS reactor.

Table 5.5: Component molar flow of all components at CO clean up-WGS section before optimization

Name	ATR Vap	HTS VAP	MTS VAP	LTS VAP
Vapour Fraction	1.00	1.00	1.00	1.00
Temperature [C]	736.71	149.75	55.10	55.01
Pressure [kPa]	101.32	101.32	101.32	101.32
Molar Flow [kgmole/h]	3301.50	3301.50	3301.50	3301.50
Comp Mole Frac (n-Octane)	0.00	0.00	0.00	0.00
Comp Mole Frac (CO)	0.24	0.21	0.21	0.21
Comp Mole Frac (Hydrogen)	0.28	0.31	0.32	0.32
Comp Mole Frac (CO2)	0.00	0.04	0.04	0.04
Comp Mole Frac (Oxygen)	0.00	0.00	0.00	0.00
Comp Mole Frac (Nitrogen)	0.44	0.44	0.44	0.44
Comp Mole Frac (H2O)	0.04	0.00	0.00	0.00
Comp Mole Frac (Carbon)	0.00	0.00	0.00	0.00
Comp Mole Frac (Methane)	0.00	0.00	0.00	0.00
Comp Molar Flow (n-Octane) [kgmole/h]	0.00	0.00	0.00	0.00
Comp Molar Flow (CO) [kgmole/h]	800.00	683.21	683.01	683.01
Comp Molar Flow (Hydrogen) [kgmole/h]	923.00	1039.79	1039.99	1039.99
Comp Molar Flow (CO2) [kgmole/h]	0.00	116.79	116.99	116.99
Comp Molar Flow (Oxygen) [kgmole/h]	0.00	0.00	0.00	0.00
Comp Molar Flow (Nitrogen) [kgmole/h]	1461.50	1461.50	1461.50	1461.50
Comp Molar Flow (H2O) [kgmole/h]	117.00	0.21	0.01	0.01
Comp Molar Flow (Carbon) [kgmole/h]	0.00	0.00	0.00	0.00
Comp Molar Flow (Methane) [kgmole/h]	0.00	0.00	0.00	0.00

5.5.2 Preferential oxidation (PROX)

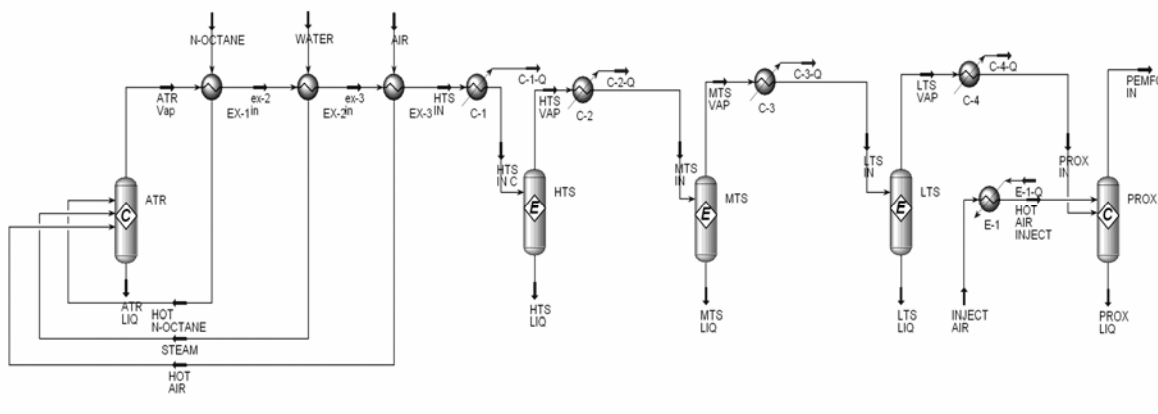


Figure 5.6: Process flow diagram of PROX

Removing carbon monoxide in a hydrogen rich stream is a critical issue and an unavoidable problem when hydrocarbons are used as the hydrogen source for fuel cells. Regardless of the reformer, small amounts of CO exist after hydrocarbon reforming and even after the WGS reaction. These small amounts of CO, typically less than 1mol%, must be removed to prevent poisoning of the fuel cell electrodes. PROX is considered as one of the most plausible and economical options. In the PROX reaction system, the following two oxidation reactions occur:



From equation (5.14) and (5.15), we can see that this process consumes an equivalent amount of hydrogen. Besides that, this process also needs oxygen to convert carbon monoxide to carbon dioxide. For this present study, the component molar flow of oxygen at inlet stream of PROX is completely used at the autothermal reformer. So there were no reactions occur at this reactor, and the amount of carbon monoxide was not reduced. This effect is evident in the results shown in table 5.6. The amount of the carbon monoxide at inlet stream (LTS VAP) and the outlet stream (PEMFC IN) of PROX is maintained at 683.01 kgmole/h and this means that PROX reaction is not occurring.

Table 5.6: The composition of all components at LTS Vap stream and PEMFC In stream

Name	LTS VAP	PEMFC IN
Vapour Fraction	1.00	1.00
Temperature [C]	55.01	55.01
Pressure [kPa]	101.32	101.32
Molar Flow [kgmole/h]	3301.50	3301.50
Comp Mole Frac (n-Octane)	0.00	0.00
Comp Mole Frac (CO)	0.21	0.21
Comp Mole Frac (Hydrogen)	0.32	0.32
Comp Mole Frac (CO ₂)	0.04	0.04
Comp Mole Frac (Oxygen)	0.00	0.00
Comp Mole Frac (Nitrogen)	0.44	0.44
Comp Mole Frac (H ₂ O)	0.00	0.00
Comp Mole Frac (Carbon)	0.00	0.00
Comp Mole Frac (Methane)	0.00	0.00
Comp Molar Flow (n-Octane) [kgmole/h]	0.00	0.00
Comp Molar Flow (CO) [kgmole/h]	683.01	683.01
Comp Molar Flow (Hydrogen) [kgmole/h]	1039.99	1039.99
Comp Molar Flow (CO ₂) [kgmole/h]	116.99	116.99
Comp Molar Flow (Oxygen) [kgmole/h]	0.00	0.00
Comp Molar Flow (Nitrogen) [kgmole/h]	1461.50	1461.50
Comp Molar Flow (H ₂ O) [kgmole/h]	0.01	0.01
Comp Molar Flow (Carbon) [kgmole/h]	0.00	0.00
Comp Molar Flow (Methane) [kgmole/h]	0.00	0.00

5.6 Plant wide optimization

As previously stated, the A/F ratio and S/F ratio is a critical parameter for ATR. For this section, we will see the effect of the S/F ratio to the whole hydrogen production plant. The air molar flow was set at its optimum value which is 1850 kgmole/h and n-octane molar flow at 100 kgmole/h. Plant wide optimization process is very important in order to determine the optimum operating conditions to achieve high hydrogen production with low carbon monoxide concentration at moderate temperature.

5.6.1 CO clean up section – WGS

The high temperature reforming reaction at the autothermal reformer, ATR, generates substantial amounts of carbon monoxide, which is converted to carbon dioxide and additional hydrogen in the water-gas shift reactors, HTS, LTS and MTS. However, even after the shift processing, high levels of CO can be present in the fuel gas, depending on the amount H_2O/C molar ratio fed into ATR and on the operating temperature of the ATR. This remaining CO must be almost completely removed in the catalytic preferential oxidizer, PROX, where it is reacted with 100% excess of oxygen.

Since this process also consumes an equivalent amount of H_2 , it is desirable to reduce the CO concentration by the shift process as much as possible, before it reaches PROX. Increasing S/F molar ratio increases the total amount of water used in the fuel processor, with a resultant decrease in the concentration of CO, and increase the production of hydrogen as stated at Eq. (5.13). This effect is evident in the results shown in Figure 5.7 and table 5.7. Figure 5.8 present the variations of the total molar flow of water versus ATR outlet temperature (HTS In temperature) after passing through the heat exchanger. Different combinations of the S/F and A/F molar ratios have an affect on the ATR outlet temperature and also HTS inlet temperature. With the intention of preventing reverse water gas shift reaction, the inlet temperature of HTS must be above

100°C. The optimum molar flow of water that being feed at ATR is 900 kgmole/h because at this point the hydrogen production is the highest (1722.18 kgmole/h) with low carbon monoxide concentration (201.90ppm) and reasonable inlet temperature of HTS (56.16°C).

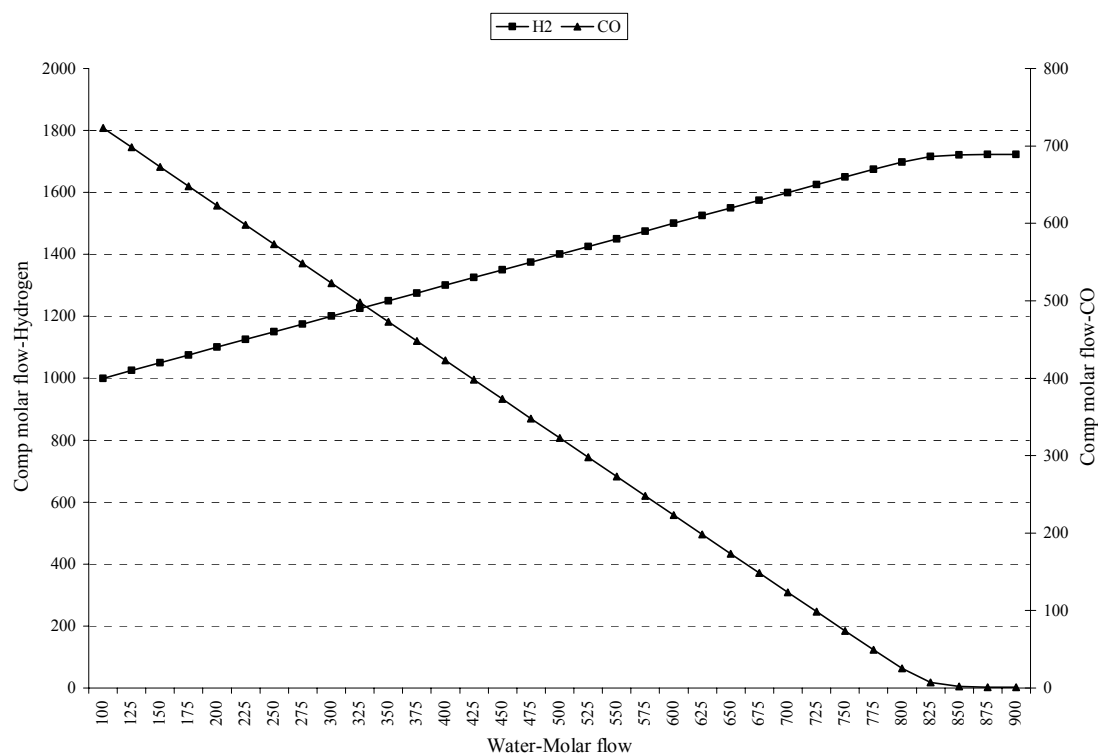


Figure 5.7: Influence of the water molar flow on the hydrogen production and CO concentration after entering WGS reactor

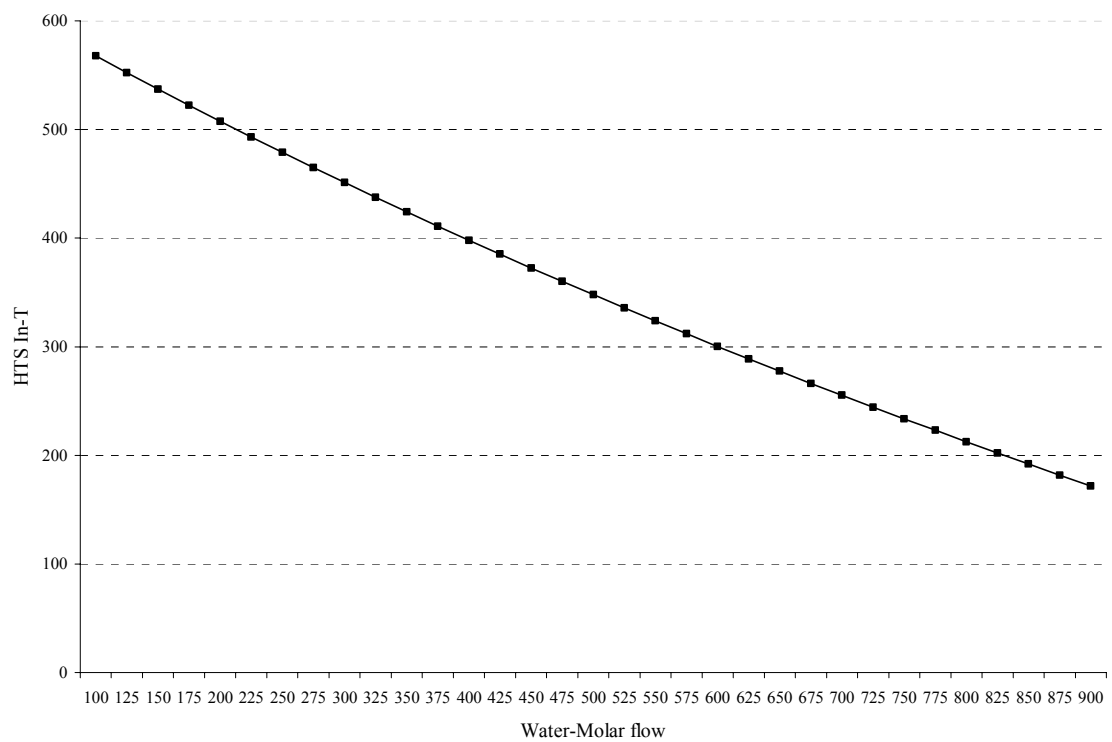


Figure 5.8: The relationship between water molar flows with HTS inlet temperature

5.6.2 CO clean up section- PROX

This level of carbon monoxide from HTS which is 201.90ppm is still too high for the fuel cell stack which can tolerate only 10 parts per million of carbon monoxide by volume in the fuel gas. The final reduction of carbon monoxide to these levels is carried out in the preferential oxidizer (PROX), where the reformat is reacted with a controlled amount of air over Au based catalysts which show good performance at lower temperature around 100°C (Choi and Stenger, 2004). The effectiveness factor for this catalyst is assumed to be 50%, i.e. of the oxygen in the injected air, one half is consumed in oxidizing the carbon monoxide to carbon dioxide, while the other half oxidizes H₂ in the fuel gas (Doss et al., 2001).

Figure 5.9 presents the influence of the amount of inject air in PROX to the concentration of carbon monoxide. From figure 5.9, the optimum value of injected air is 50 kgmole/h, because at this point the concentration of carbon monoxide is below 10 ppm, which is 7.32 ppm. On the other hand, the inlet temperature of the PEMFC is reasonable at this optimum value which is 94.85°C which can be seen in Table 5.8. Table 5.8 presents the comparison of the composition in PEMFC In before and after optimization.

The most commonly used membrane in PEMFC is Nafion® by DuPont®, which relies on liquid water humidification of the membrane to transport protons. This implies that it is not feasible to use temperatures above 100°C, since the membrane would dry (Joensen et al., 2002). However, the ideal fuel for PEMFC is pure hydrogen, with less than 10 ppm carbon monoxide, as dictated by the poisoning limit of the Pt fuel cell catalyst.

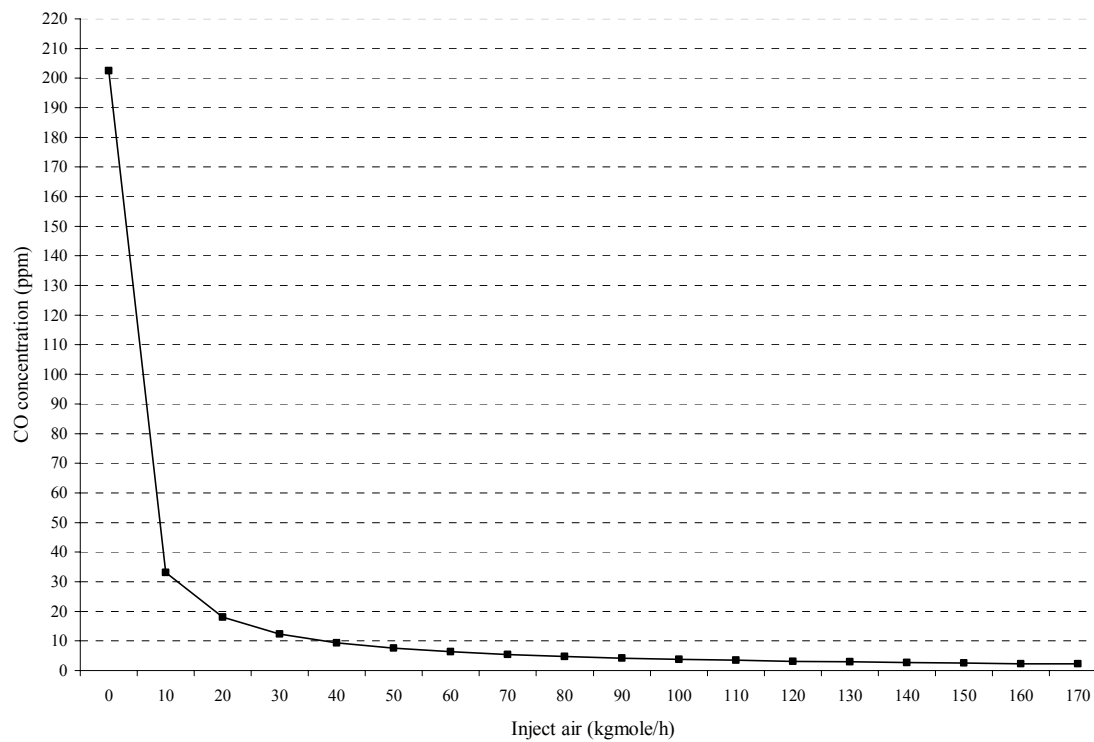


Figure 5.9: Influence of the inject air molar flow in PROX on the CO concentration after entering PROX

Table 5.8: Comparison of the composition in PEMFC In before and after optimization

Name	PEMFC In	
	Before	After
Vapour Fraction	1.00	1.00
Temperature [C]	100.00	94.85
Pressure [kPa]	101.32	101.32
Molar Flow [kgmole/h]	3992.00	4101.00
Comp Mole Frac (n-Octane)	0.00000	0.00000
Comp Mole Frac (CO)	0.00282	0.00001
Comp Mole Frac (Hydrogen)	0.43406	0.41501
Comp Mole Frac (CO2)	0.19758	0.19507
Comp Mole Frac (Oxygen)	0.00000	0.00000
Comp Mole Frac (Nitrogen)	0.35621	0.36601
Comp Mole Frac (H2O)	0.00933	0.02390
Comp Mole Frac (Carbon)	0.00000	0.00000
Comp Mole Frac (Methane)	0.00000	0.00000
Comp Molar Flow (n-Octane) [kgmole/h]	0.00	0.00
Comp Molar Flow (CO) [kgmole/h]	11.24	0.03
Comp Molar Flow (Hydrogen) [kgmole/h]	1732.76	1701.97
Comp Molar Flow (CO2) [kgmole/h]	788.76	799.97
Comp Molar Flow (Oxygen) [kgmole/h]	0.00	0.00
Comp Molar Flow (Nitrogen) [kgmole/h]	1422.00	1501.00
Comp Molar Flow (H2O) [kgmole/h]	37.24	98.03
Comp Molar Flow (Carbon) [kgmole/h]	0.00	0.00
Comp Molar Flow (Methane) [kgmole/h]	0.00	0.00

5.7 Temperature profile of fuel processor system

The temperature profile of the fuel processor is illustrated in Figure 5.10. Air, water and n-octane were heated up to 150 °C before entering ATR. With 18.5 of A/F and 9.0 of S/F ratios, the outlet temperature of ATR reactor is about 736.71°C which is practical to suppress CH₄-formation in the ATR (Springmann et al., 2004). After that, the effluent is then cooled to 562.8°C, 226.5°C and 171.9°C by passing it through EX-1, EX-2 and EX-3, respectively. The temperature then needs to be decrease to 100 °C before entering the HTS to prevent reversible reaction happened in Eq. (5.13). In the HTS, the inlet temperature is 100°C, whereas the outlet temperature is about 312.94°C. The increased in the outlet temperature is due to the exothermic nature of WGS reaction.

The same profile is shown by MTS and LTS. The outlet temperature of HTS, MTS and LTS are cooled down to 55 °C before entering MTS, LTS and PROX reactor which is for the same reason with HTS reactor. The outlet temperature of HTS and LTS are slightly increased to 98.68 °C and 56.15 °C due to the exothermic nature of WGS reaction. There is also slightly increased in the outlet temperature of the PROX reactor, but this is due to the exothermic of PROX reaction (Eqs. 5.14-5.15). The outlet temperature of PROX reactor is 94.85 °C, which is in the range of operating temperature for PEMFC as mentioned by Joensen et al. (2002).

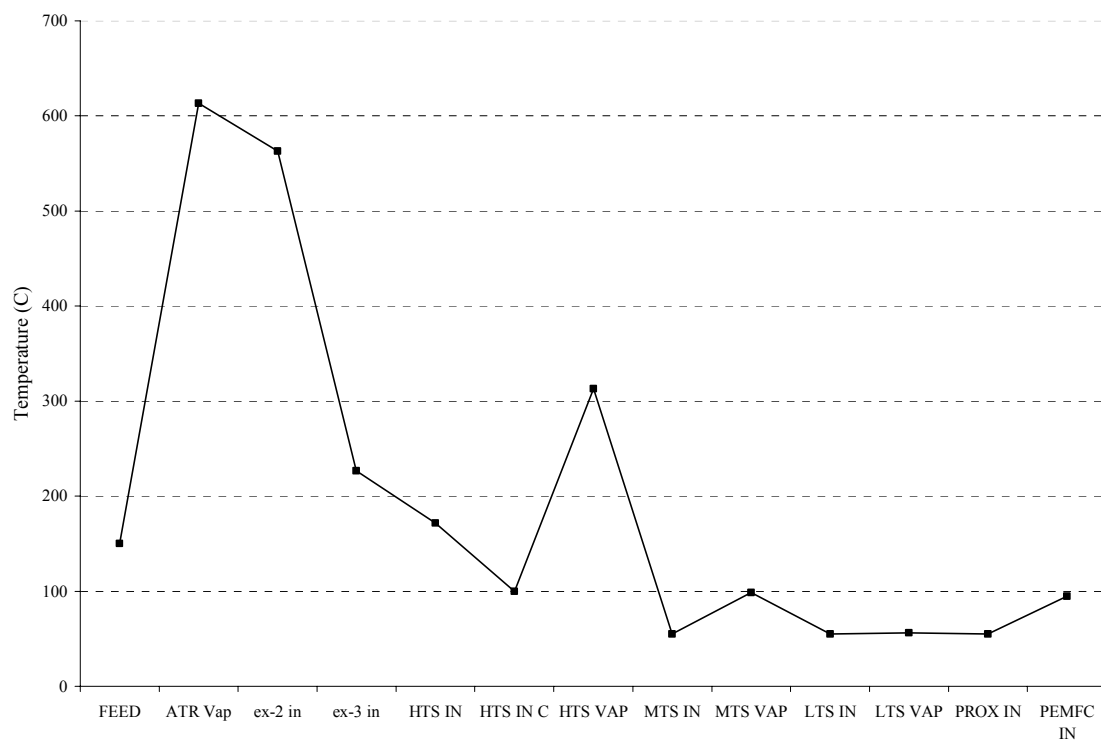


Figure 5.10: Temperature profile of fuel processor system

5.8 Molar fraction profile of fuel processor system

Fuel processing system consists of an autothermal reformer (ATR), where gasoline is converted into a hydrogen-rich gas, and several subsequent gas-cleaning stages, like HTS, MTS, LTS and PROX reactors. Figure 5.11 shows the behavior of hydrogen and carbon monoxide of the fuel processor system from ATR to PROX reactors. The molar fraction profile for all components is attached at appendix. The aim of this study is to maximize the production of hydrogen and in the same time to get the carbon monoxide concentration below 10 ppm. For that reason, it is important to observe the molar fraction profile of carbon monoxide and hydrogen.

As shown Figure 5.11, the concentration behavior of hydrogen and CO after the ATR is contrary. This is because, immediately after the ATR, is a CO clean-up system where the hydrogen-rich syngas goes through a series of reactors to perform the water gas shift reaction in which CO is converted into CO₂ and hydrogen with the existence of steam. For that, the concentration of CO is almost zero in the outlet of LTS. After passing through the PROX reactor, the concentration of CO is zero while the hydrogen concentration also slightly decreases due to PROX reactions in which converted CO to CO₂ and hydrogen to water with the existence of air.

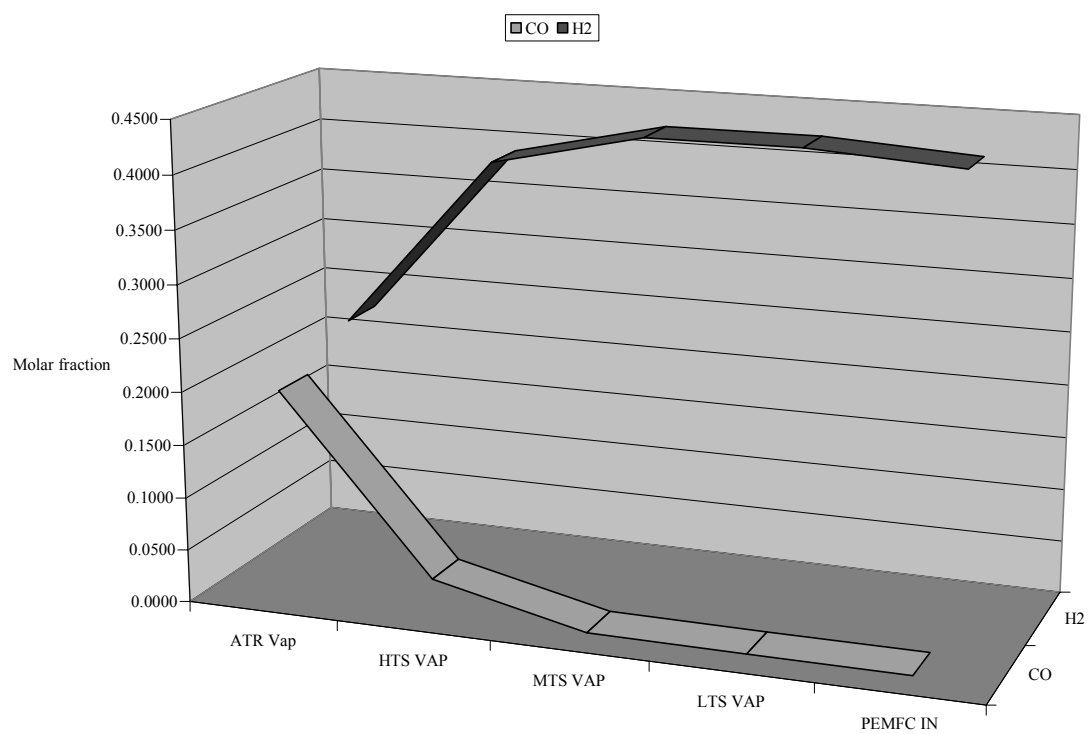


Figure 5.11: Molar fraction profile of CO and hydrogen of fuel processor system

5.9 Process efficiency

To be an alternative to modern combustion engines, fuel cell systems with hydrogen production by gasoline reforming have to enable higher efficiencies than internal combustion engines in order to lower the fuel consumption of modern cars. The efficiency of the fuel processor is defined as

$$\text{Efficiency}(\%) = \eta = \frac{(n_{H_2} LHV_{H_2}) + (n_{CO} LHV_{CO})}{n_{C_xH_y} LHV_{C_xH_y}} \times 100 \quad (5.16)$$

The lower heating value for hydrogen and carbon monoxide is constant parameters and we can get it from the journal. The lower heating value for hydrogen and carbon monoxide are:

Table 5.9: Lower heating value for hydrogen and carbon monoxide
(Lenz and Aicher, 2005)

Component	Lower heating value (LHV) (kJ/mol)
Hydrogen	241.83
Carbon monoxide	282.00

While the value of LHV of fuel used is 5.119×10^6 kcal/kgmole that we can get it straight from the simulator. So, the efficiency of the fuel processor system is:

$$\begin{aligned} \eta &= \frac{(1701.97 \times 241.83) + (0.03 \times 282.00)}{100 \times (5.119 \times 10^6)} \times 100 \\ &= 80.41\% \end{aligned}$$

5.10 Summary

The simulation of catalytic autothermal reforming of gasoline to produce hydrogen for fuel cell applications has been developed. By optimisation, the results presented show how the operating conditions of ATR, A/F and S/F ratios influence the hydrogen production, CO concentration and fuel processor efficiency. The results of the simulation and optimisation are summarized below.

- 1) The autothermal reforming reactor temperature is greatly influence by the difference between the A/F ratio and S/F ratio. This is due to the exothermic reaction of partial oxidation and endothermic reaction of steam reforming.
- 2) Heat integration is one of the economical ways to decrease the utilization of utilities such as steam and at the same time give high efficiency to the fuel processor.
- 3) CO concentration can be reduced by water-gas shift and preferential oxidation reaction by utilizing water and excess air. Higher amount of water used in the fuel processor lead to lower concentrations of CO at the exit from the low-temperature water-gas shift reactor (Figure 5.7). This decreases the CO removal duty of the preferential oxidation unit.
- 4) The fuel processor efficiency is slightly affected by reducing or increasing the A/F ratio. When A/F ratio is higher, the fuel processor efficiency will decrease, and this is based on Eq. 5.17.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

There are a lot of research that had been carried out to produce hydrogen from gasoline via different methods such as SREF, POX and ATR. From the literature study, the hydrogen production from ATR seem to be the most promising concept for mobile applications because the reactor design is much simpler (smaller and lighter unit), than that of conventional steam reformer with internal heat exchanger. Besides of that, it also offers advantages of lower operating temperature, flexible load following characteristics as compared to the SREF process and has higher energy efficiency than the POX process. The ATR of n-octane involves a complex set of chemical reactions such as total oxidation, partial oxidation, steam reforming, methanation, CO₂ reforming, cracking, boudouard and carbon gasification.

The simulation of autothermal reforming of gasoline to produce hydrogen for fuel cell applications has been developed. The PEM fuel cell system consists of two major subsystems, namely fuel processing and fuel cell. Fuel processing consists of reforming and clean-up sections. The reforming section contains the reforming reactor, an ATR while the clean up section is made up by high, medium and low temperature shift reactors (HTS, MTS and LTS) and the preferential oxidation reactor (PROX). The ATR and preferential oxidation (PROX) processes is modeled using conversion reactor, while the water gas shift (WGS) process is modeled using equilibrium reactor within HYSYS environment. By optimisation, the results presented show how the operating conditions of ATR, A/F and S/F ratios influence the hydrogen production, CO concentration and fuel processor efficiency. The fuel processor efficiency is slightly affected by reducing or increasing the A/F ratio. When A/F ratio is higher, the fuel processor efficiency will decrease, and this is based on Eq. 5.17.

6.2 Conclusions

A number of important observations were noted based on the analyses of results as presented in the previous chapter. The main contributions of this research to the simulation of hydrogen production plant for fuel applications, which also represent the new developments in this field, are the following:

1. The simulation of hydrogen plant model using ATR of gasoline had been successfully developed using Aspen HYSYS 2004.1.
2. The optimum A/F and S/F ratios are 18.5 and 9.0 respectively to produce 42% hydrogen and 7.56 ppm of CO.

3. With optimum parameters above, 80.41% of fuel processor efficiency was achieved.

6.3 Recommendations

There are several recommendations in order to improve the performance of the fuel cells for the future study.

1. Purification of hydrogen

It is obvious that the product gas mixture exiting the ATR reaction system contains appreciable amounts of water vapor, carbon dioxide, and nitrogen as well as the desired hydrogen product. In view of compactness requirements and the need for a robust hydrogen generation system to be integrated with the fuel cell system in the future proposed mobile applications, a hydrogen purification step becomes inevitable.

2. Water management

One of the objectives of the fuel processor system is to maintain self-sufficiency with respect to water needs. In each of the systems, there is a single exhaust stream consisting of CO₂ and water vapor from the complete combustion of the fuel, a small amount of unused oxygen, and all of the nitrogen that originates with air feed streams. Recovery of sufficient water from the exhaust stream to meet the steam generation needs depends on the following four factors:

- Exhaust temperature. The cooler the exhaust, the more water is recovered by condensation. The minimum temperature is limited by ambient temperature and the amount of heat transfer surface area.

- Exhaust pressure. Higher pressures allow more water condensation, but require an increase in the fuel cell operating pressure.
- Air feed rate. The more air that is fed to the system, the more nitrogen must be purged out with the exhaust. More exhaust nitrogen reduces the recovery of water condensed from the exhaust. There are two sources of air feed: (i) air to autothermal reformer, and (ii) air to the PROX reactor. These air rates are determined by stoichiometric ratios, which are not varied for the sake of the water balance.
- Fuel processor efficiency. As the fuel processor efficiency is reduced, the hydrocarbon feed rate to the processor is increased. This increases the production of water vapor, since all hydrocarbon is eventually combusted completely. With all else held constant, the additional water production will be recovered in the exhaust condenser.

3. Dynamic analysis

Polymer electrolyte membrane (PEM) fuel cells are considered as one of the most promising technology to replace the internal combustion engines in vehicles. However, in order for these fuel processor/ fuel cell vehicles to be commercially successful, issues such as start time and transient response must be addressed. Cold start time and cold start fuel consumption is probably the most difficult issue to be solved. So, the researches have to be done on the role of transient response of the fuel processor in the overall system architecture and how it relates to efficiency and emissions of a gasoline fuel cell vehicle. This issues is relates to the dynamic performance of the fuel processor.

REFERENCES

- Aartun, I., Venvik, H.J., Holmen, A., Pfeifer, P. and Gorke, O. (2005). "Temperature Profiles and Residence Time Effects during Catalytic POX and Oxidative SR of Propane in Metallic Microchannel Reactors." *Catalysis Today*. **110**. 98-107.
- Agosta, A., Cernansky, N.P., Miller, D.L., Faravelli, T. and Ranzi, E. (2004). "Reference Components of Jet Fuels: Kinetic Modeling and Experimental Results." *Experimental Thermal and Fluid Science*. **28**. 701–708.
- Ahmed, S., Ahluwalia, R., Lee, S.H.D. and Lottes, S. (2006). "A Gasoline Fuel Processor Designed to Study Quick-Start Performance." *Journal of Power Sources*. **154**. 214-222.
- Avci, A.K., Onsan, Z.I. and Trimm, D.L. (2001). "On Board Fuel Conversion for Hydrogen Fuel Cells: Comparison of Different Fuels by Computer Simulations." *Applied Catalysis A: General* **216**. 243-256.
- Avci, A.K., Trimm, D.L. and Aksoylu, A.E., Onsan, Z.I. (2004). "Hydrogen Production by Steam Reforming of n-Butane over Supported Ni and Pt-Ni Catalysts." *Applied Catalysis A: General* **258**. 235-240.

- Barbir, F. (2005). "PEM Electrolysis for Production of Hydrogen from Renewable Energy Sources. *Solar Energy*. **78**. 661-669.
- Biniwale, R.B., Mizuno, A. and Ichikawa, M. (2004). "Hydrogen Production by Reforming of Iso-Octane Using Spray-Pulsed Injection and Effect of Non-Thermal Plasma." *Applied Catalysis A: General* **276**. 169–177.
- Brown, L.F. (2001). "A Comparative Study of Fuels for on-Board Hydrogen Production for Fuel-Cell-Powered Automobiles." *International Journal of Hydrogen Energy*. **26**. 381–397.
- Cheng, Z. Y., Lu, C.W., Yong, M.L., Gui, S.W., Yong, C., Wei, L.D. and He, Y.H. (2006). "Effects of Preparation Method on the Hydrogen Production from Methanol SR over Binary Cu/ZrO₂ Catalysts. *Applied Catalysis A. General* **297**. 151-158.
- Choi, Y. and Stenger, H.G. (2004). "Kinetics, Simulation and Insights for CO Selective Oxidation in Fuel Cell Applications." *Journal of Power Sources*. **129**. 246-254.
- Constantino, U., Marmottini, F., Sisani, M., Montanari, T., Ramis, G., Busca, G., Turco, M. and Bagnasco, G. (2005). "Cu-Zn-Al Hydrotalcites as Precursors of Catalysts for the Production of Hydrogen from Methanol." *Solid State Ionics*. **176**. 2917-2922.
- Dagaut, P. and Cathonnet, M. (2006). "The Ignition, Oxidation, and Combustion of Kerosene: A Review of Experimental and Kinetic Modeling." *Progress in Energy and Combustion Science*. **32**. 48–92
- Dong, J.M., Sreekumar, K., Sang, D. L., Byung, G. L. and Hoon, S.K. (2001). "Studies on Gasoline Fuel Processor System for Fuel-Cell Powered Vehicles Application." *Applied Catalysis A: General* **215**. 1– 9.

- Doss, E.D., Kumar, R., Ahluwalia, R.K. and Krumpelt, M. (2001). "Fuel Processors for Automotive Fuel Cell Systems: A Parametric Analysis." *Journal of Power Sources*. **102**. 1-15.
- Erickson, P.A. (2004). "Hydrogen Production for Fuel Cells via Reforming Coal Derived Methanol." Technical Report **823769**.100-116.
- Ersoz, A., Olgun, H. and Ozdogon, S. (2005). "Simulation Study of a Proton Exchange Membrane (PEM) Fuel Cell System with Autothermal Reforming." *Energy*. Article in Press. 1-11.
- Ersoz, A., Olgun, H. and Ozdogon, S. (2006). "Reforming Options for Hydrogen Production from Fossil Fuels for PEM Fuel Cells." *Journal of Power Sources*. **154**. 67-73.
- Ersoz, A., Olgun, H., Ozdogon, S., Gungor, C., Akgun, F. and Tiris, M. (2003). "Autothermal Reforming as a Hydrocarbon Fuel Processing Option for PEM Fuel Cell." *Journal of Power Sources*. **118**. 384-392.
- Feg, W.C., Hsin, Y.Y., Roselin, L.S. and Hsien, C.Y. (2006). "Production of Hydrogen via POX of Methanol over Au/TiO₂ Catalysts." *Applied Catalysis A. General* **290**. 138-147.
- Fernandez, E.O., Rusten, H.K., Jakobsen, H.A., Ronning, M. and Holmen, A. (2005). "Sorption Enhanced Hydrogen Production by SMR using Li₂ZrO₃ as Sorbent: Sorption Kinetics and Reactor Simulation. *Catalysis Today*. **106**. 41-46.
- Frias, J.M., Pham, A.Q. and Aceves, S.M. (2003). "A Natural Gas –Assisted Steam Electrolyzer for High Efficiency Production of Hydrogen." *International Journal of Hydrogen Energy*. **28**. 483-490.

- Fukahori, S., Kitaoka, T., Tomoda, A. and Suzuki, R. (2006). "Methanol SR over Paper-Like Composites of Cu/ZnO Catalyst and Ceramic Fiber." *Applied Catalysis A. General* **300**. 155-161.
- Granovskii, M., Dincer, I. and Rosen, M.A. (2006). "Life Cycle Assessment of Hydrogen Fuel Cell and Gasoline Vehicles." *International Journal of Hydrogen Energy*. **31**. 337 – 352.
- Grosjean, M.H., Zaloumi, M., Hout, J.Y. and Roue, L. (2005). "Hydrogen Generation via Alcoholysis Reaction using Ball-Milled Mg Based Materials. *International Journal of Hydrogen Energy*. **87**. 1-12.
- Gu, G.P., Sung, D.M., Young, G.Y., Chang, S.K., Dong, J.S. and Koichi, E. (2005). "Hydrogen Production with Integrated Micro Channel Fuel Processor using Methanol for Portable Fuel Cell Systems." *Catalysis Today*. **110**. 108-113.
- Hamid, M.K.A, Ibrahim, N., Ibrahim, K.A. and Ahmad, A. (2006). "Simulation of Hydrogen Production for Mobile Fuel Cell Applications via Autothermal Reforming of Methane." *Proceedings of the 1st International Conference on Natural Resources Engineering & Technology 2006*. 540-548
- Hey, K.L., Kalk, T., Mahlendorf, F., Niemzig, O. and Roes, J. (2004). "Portable PEFC Generator with Propane as Fuel." *Journal of Power Sources*. **86**. 166-172.
- Hoang, D.L., Chan, S.H. and Ding, O.L. (2006). "Hydrogen Production for Fuel Cells by ATR of Methane over Ni/SiO₂ Catalysts." *Applied Catalysis A. Volume* **300**. 8-13.
- Joensen, F. and Nielsen, J.R.R. (2002). "Conversion of hydrocarbons and alcohols for fuel cells." *Journal of Power Sources*. **105**. 195-201.

- Kusakabe, K., Fumio, S., Eda, T., Oda, M. and Sotowa, K. (2005). "Hydrogen Production in Zirconia Reactors for Use in PEM Fuel Cells." *International Journal of Hydrogen Energy*. Volume **9**. 989-994.
- Laosiripojana, N. and Assabumrungrat, S. (2005). "Hydrogen Production from Steam and ATR of LPG over High Surface Area Ceria." *Journal of Power Sources*. 1-10.
- Lee, S.H.D., Applegate, D.V., Ahmeda, S., Calderoneb, S.G. and Harvey, T.L. (2005). "Hydrogen from Natural Gas: Part I—Autothermal Reforming in an Integrated Fuel Processor." *International Journal of Hydrogen Energy*. **30**. 829 – 842.
- Lenz, B. and Aicher, T. (2005). "Catalytic Autothermal Reforming of Jet Fuel." *Journal of Power Sources*. **149**. 44-52
- Mattos, L.V., Noronha, F.B. "Hydrogen Production for Fuel Cell Applications by Ethanol POX on Pt/CeO₂ Catalysts: The Effect of the Reaction Conditions and Reaction Mechanism." *Journal of Catalyst*. **233**. 453-463.
- Minutillo, M. (2005). "On-Board Fuel Processor Modelling for Hydrogen-Enriched Gasoline Fuelled Engine." *International Journal of Hydrogen Energy*. **30**. 1483 – 1490.
- Mizuno, T., Matsumura, Y., Nakajima, T. and Mishima, S. (2003). "Effect of Support on Catalytic Properties of Rh Catalysts for Steam Reforming of 2-Propanol." *International Journal of Hydrogen Energy*. **28**. 1393-1399.
- Mjaanes, H.P., Chan, L. and Mastorakos, L. (2005). "Hydrogen Production from Rich Combustion in Porous Media." *International Journal of Hydrogen Energy*. **30**. 579 – 592.

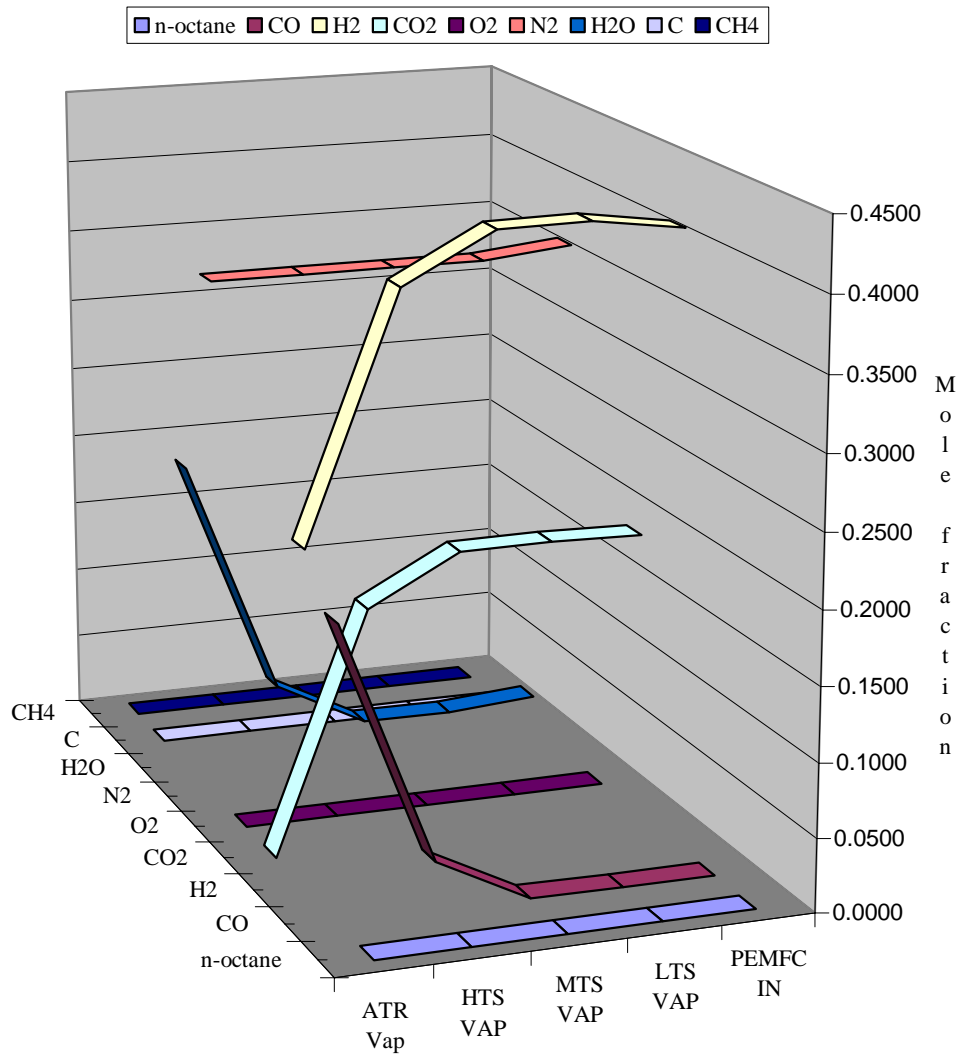
- Otsuka, K., Shigeta, Y. and Takenaka, S. (2002). "Production of Hydrogen from Gasoline Range Alkanes with Reduced CO₂ Emission." *International Journal of Hydrogen Energy*. **27**. 11–18.
- Peters, R., Dusterwald, H.G. and Hohlein, B. (2000). "Investigation of a Methanol Reformer Concept Considering the Particular Impact of Dynamics and Long Term Stability for Use in a Fuel Cell Powered Passenger Car." *Journal of Power Sources*. **86**.507-514.
- Qijan, Z., Xiaohong, L., Fujimoto, K. and Asami, K. (2005). "Hydrogen Production by POX and SR of DME." *Applied Catalysis A*. Volume **288**. 169-174.
- Resini, C., Arrighi, L., Delgado, M.C.H., Vargas, M.A.L. and Busca, G. (2006). "Production of Hydrogen by SR of C₃ Organics over Pd-Cu/Al₂O₃ Catalyst." *International Journal of Hydrogen Energy*. **31**. 13-19.
- Reuse, P., Ranken, A., Santo, K.H., Oliver, G. and Schubert, K. (2004). "Hydrogen Production for Fuel Cell Application in an Autothermal Micro-Channel Reactor." *Chemical Engineering Journal*. **101**. 133-141.
- Shetian, L., Takahashi, K., Fuchigami, K. and Uematsu, K. (2006). "Hydrogen Production by Oxidative Methanol Reforming on Pd/ZnO: Catalyst deactivation." *Applied Catalyst A. General* **299**. 58-65.
- Shetian, L., Takashi, K., Uematsu, K. and Ayabe, M. "Hydrogen Production by Oxidative Methanol Reforming on Pd/ZnO." *Applied Catalysis A*. Volume **283**. 125-135.

- Shoko, E., McLellan, B., Dicks, A.L. and Costa, J.C.D. (2006). "Hydrogen from Coal: Production and Utilisation Technologies." *International Journal of Coal Geology*. **65**.213-222.
- Silva, C.F., Ishikawa, T., Santos, S., Alves Jr, C. and Martinelli, A.E. (2006). "Production of Hydrogen from Methane using Pulsed Plasma and Simultaneous Storage in Titanium Sheet." *International Journal of Hydrogen Energy*. **31**. 49 – 54.
- Sommer, M., Lamm, A., Docter, A. and Agar, D. (2004). "Modelling and Dynamic Simulation of Fuel Cell System with an Autothermal Gasoline Reformer." *Journal of Power Sources*. **127**. 313-318.
- Soo, Y.C., Ya, H.C. and Amiridis, M.D. (2006). "Hydrogen Production via the Catalytic Cracking of Ethane over Ni/SiO₂ Catalysts. *Applied Catalysis A. General* **300**. 8-13.
- Springmann, S., Bohnet, M., Docter, A., Lamm, A. and Eigenberger, G. (2004). "Cold Start Simulation of a Gasoline Based Fuel Processor for Mobile Fuel Cell Applications." *Journal of Power Sources*. **128**. 13-24.
- Springmann, S., Friedrich, G., Himmen, M., Sommer, M. and Eigenberger, G. (2002). "Isothermal Kinetic Measurements for Hydrogen Production from Hydrocarbon Fuels Using a Novel Kinetic Reactor Concept." *Applied Catalysis A: General* **235**. 101-111.
- Suelves, I., Lázaro, M.J., Molinera, R., Corbella, B.M. and Palacios J.M. (2005). "Hydrogen Production by Thermo Catalytic Decomposition of Methane on Ni-Based Catalysts: Influence of Operating Conditions on Catalyst Deactivation and Carbon Characteristics." *International Journal of Hydrogen Energy*. **30**. 1555 – 1567.

- Suzuki, T., Iwanami, H.I. and Yoshinari, T. (2000). "Steam Reforming of Kerosene on Ru/Al₂O₃ Catalyst to Yield Hydrogen." *International Journal of Hydrogen Energy*. **25**. 119±126.
- Thomas, C.E., James, B.D., Lomax Jr, F.D. and Kuhn Jr, I.F. (2000). "Fuel Options for the Fuel Cell Vehicle: Hydrogen, Methanol or Gasoline?" *International Journal of Hydrogen Energy*. **25**. 551-567.
- Trimm, D.L., Adesina, A.A., Praherso and Cant, N.W. (2004). "The Conversion of Gasoline to Hydrogen for On-Board Vehicle Applications." *Catalysis Today*. **93–95**. 17–22.
- Villegas, L., Guilhaume, N., Provendier, H., Daniel, C., Masset, F. and Mirodatos, C. (2005). "A Combined Thermodynamic/Experimental Study for the Optimisation of Hydrogen Production by Catalytic Reforming of Isooctane." *Applied Catalysis A. General* **281**. 75-83.
- Wang, L., Murata, K. and Megumu, I. (2003). "Production of Pure Hydrogen and More Valuable Hydrocarbons from Ethane on a Novel Highly Active Catalyst with a Pd-based Membrane Reactor." *Volume* **82**. 99-104.
- Wang, Y. and Wu, D. (2001). "The Experimental Research for Production of Hydrogen from n-Octane through Partially Oxidizing and Steam Reforming Method." *International Journal of Hydrogen Energy*. **26**. 795–800.
- Wang, Y.H. and Zhang, J.C. (2005). "Hydrogen Production on Ni-Pd-Ce/ γ -Al₂O₃ Catalyst by Partial Oxidation and Steam Reforming of Hydrocarbons for Potential Application in Fuel Cells." *Fuel*. **84**. 1926-1932.

- Wiese, W., Emonts, B. and Peters, R. (1999). "Methanol SR in a Fuel Cell Drive System. *Journal of Power Sources*. **84**.187-193.
- Xinhai, Y., Shan, T.T., Zhengdong, W. and Yunshi, Q. (2005). "On Board Production Hydrogen for Fuel Cells over Cu/ZnO/Al₂O₃ Catalyst Coating in a Micro Channel Reactor." *Journal of Power Sources*.**150**. 57-66.
- Xu, Y., Kameoka, S., Kishida, K., Demura, M., Tsai, A.P. and Hirano, T. (2005). "Catalytic Properties of Alkali-Leached Ni₃Al for Hydrogen Production from Methanol." *Intermetallics*. **13**. 151-155.
- Yi, N.W. and Rodrigues, A.E. (2005). "Hydrogen Production from Steam Methane Reforming Coupled with In Situ CO₂ Capture: Conceptual Parametric Study." *Fuel*. **84**. 1778-1789.
- Zhou, Z.F., Gallo, C., Pague, M.B., Schobert, H. and Lvov, S.N. (2004). "Direct Oxidation of Jet Fuels and Pennsylvania Crude Oil in a Solid Oxide Fuel Cell." *Journal of Power Sources*. **133**.181–187.

Appendix A



Molar fraction profile of all components from ATR to PROX reactor