OPTIMIZATION OF JET FUEL AUTOTHERMAL REFORMER FOR FUEL CELL APPLICATIONS

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Thanks to God, my beloved parents and family, my esteemed advisor and not forgetting my fellow friends…

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ABSTRACT

Fuel cell is an electrochemical device that converts hydrogen and oxygen into electricity without combustion. In this research jet fuel is converted to hydrogen for fuel cell application via autothermal reforming process. The autothermal reforming process consist of three different processes which are total oxidation (TOX) and partial oxidation (POX) processes, steam reforming (SR) process, water-gas shift (WGS) process and preferential oxidation (PROX) process. Jet fuel, air or oxygen and water were fed first to the conversion reactor for the reforming process then to the equilibrium reactor for the water-gas shift process to occur. Finally, to the conversion reactor where the preferential oxidation process takes place. The base case simulation model of the hydrogen production plant was developed based on the understanding of the process. The steady-state simulation was developed using Aspen HYSYS 2004.1. Optimization of the plant was carried out phase by phase to get the optimum value of water and air should be fed into the ATR reactor at 100 kgmole/h of jet fuel. The optimum ratios for air-to-fuel (A/F) and steam-to-fuel (S/F) are 35 and 18 respectively, to produce 39.4% of hydrogen and less than 10 ppm of CO with 80.4% of fuel processor efficiency.

ABSTRAK

Sel bahan api adalah sejenis alat elektrokimia yang menukarkan gas hidrogen dan oksigen kepada tenaga elektrik tanpa pembakaran. Dalam penyelidikan ini, kerosen ditukarkan kepada hidrogen untuk aplikasi sel bahan api melalui proses *autothermal reforming*. Proses *autothermal reforming* ini mengandungi tiga proses berlainan iaitu proses pengoksidaan penuh (TOX) dan pengoksidaan sebahagian (POX), proses *steam reforming* (SR) dan proses penukaran air-gas (WGS) dan proses *preferential oxidation* (PROX). Kerosen, udara atau oksigen dan oksigen disuap masuk ke dalam reaktor penukaran untuk menjalankan proses *reforming* dan kemudiannya ke dalam reaktor keseimbangan untuk menjalankan proses penukaran air-gas. Setelah itu ia ke reaktor penukaran di mana proses *preferential oxidation* berlaku. Simulasi model pelan penghasilan hidrogen pada keadaan tetap dibina berdasarkan pemahaman terhadap keseluruhan proses. Model ini dibina mengunakan perisian simulasi komputer Aspen HYSYS 2004.1. Setelah itu model ini dioptimumkan untuk mendapatkan nilai suapan air dan udara yang optimum untuk dimasukkan ke dalam reaktor *autothermal reforming* pada suapan kerosen sebanyak 100 kgmol/jam. Nilai optimum yang diperolehi bagi nisbah udara kepada bahan api dan wap air kepada bahan api adalah masing-masing 35 dan 18. Manakala sebanyak 39.4% hidrogen dihasilkan dengan isipadu CO kurang dari 10 ppm. Kecekapan pemprosesan bahan api pula adalah sebanyak 80.4%.

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LIST OF SYMBOLS

λ	-	Air to fuel ratio
Al	-	Aluminium
ANL	-	Argonne National Laboratory
ATR	-	Autothermal Reforming
C	-	Carbon
CO_2	-	Carbon Dioxide
CO	-	Carbon Monoxide
CSTR	-	Continuously Stirred Tank Reactor
^oC	-	degree Celcius
ft^3	-	cubic feet
g/L	-	gram per litre
$gmol^{-1}$	-	gram per mol
GHSV	-	Gas Hourly Space Velocity
h	-	hour
H	-	Hydrogen(atom)
HCs	-	Hydrocarbons
H_2	-	Hydrogen(molecule)
H_2O	-	Water
K	-	Kelvin
$kJ\ mol^{-1}$	-	kilo Joule per mol
kW	-	kilo Watt
LHSV	-	Liquid Hourly Space Velocity
LHV	-	Lower Heating Value
mol/h	-	mol per hour
m^3	-	cubic meter

m^3/h	-	cubic meter per hour
Ni	-	Nickel
O_2	-	Oxygen(molecule)
ODE	-	Ordinary Differential Equation
P	-	Pressure
PEMFC	-	Proton Exchange Membrane Fuel Cell
POX	-	Partial Oxidation
PROX	-	Preferential Oxidation
Ru	-	Ruthenium
RXNEQ	-	a thermodynamics equilibrium computer code developed by Haynes(1990)
S/C	-	Steam to carbon ratio
Si	-	Silica
SR	-	Steam-Reforming
STP	-	standard temperature and pressure [298.15 K and 101.325 kPa (1 atm)]
TOX	-	Total Oxidation
w	-	work
WGS	-	Water Gas Shift

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CHAPTER I

INTRODUCTION

1.3 Background Information

Hydrogen is a chemical that can be produced using any primary energy source. Its use as a fuel could lead to lower emissions of pollutants and greenhouse gases. Further, depending on which primary energy supply is used, hydrogen fuel could help reduce energy imports, especially for transportation. A major use of hydrogen would be in fuel cells (Lenz et al., 2005).

One very promising technology that has received increasing attention because of its ability to increase overall energy efficiency is fuel cells. Simply put, a fuel cell is an electrochemical device that converts hydrogen and oxygen into electricity without combustion. Fuel cells have been around since the mid 19^{th} century, and the space program has used them since the early 1960s. A fuel cell operates much like a battery, turning oxygen and hydrogen into electricity in the presence of an electrically conductive material called an electrolyte. But unlike a battery, it never loses its charge and will generate electricity as long as there is a source of hydrogen and oxygen (KCC Energy Website).

As said before fuel cell is a device that produces electricity through a chemical process, as opposed to combustion. Fuel cells have the potential to achieve significantly higher efficiencies (i.e. produce more power for a given energy input) than combustion engines and conventional power plants. They can be refuelled at anytime, and do not run down or need to be recharged, making them similar to combustion engines in their use. However, fuel cells utilize chemical processes that are inherently more efficient than combustion. For example, a typical combustion-based fossil fuel power plant operates at about 35% efficiency, while a fuel cell electricity generator can operate at 40 to 60% efficiency. As such, fuel cells could potentially provide energy more cleanly and efficiently than combustion engines (Culture Change Website).

One key advantage of using hydrogen as a fuel is that virtually any primary energy source can be used to generate it. A major motivation for the hydrogen economy is the potential to use environmentally benign, domestic, and/or sustainable energy sources. Hydrogen can be produced either by reforming hydrocarbon fuels or by splitting water. Hydrocarbon fuels include fossil fuels (crude oil, coal, and natural gas) and biomass such as alcohol (e.g. methanol produced from landfill methane or ethanol produced from corn) (KCC Energy Website).

Typical reactants used in a fuel cell are hydrogen on the anode side and oxygen on the cathode side (a hydrogen cell). Typically in fuel cells, reactants flow in and reaction products flow out, and continuous long-term operation is feasible virtually as long as these flows are maintained. Fuel cells are often considered to be very attractive in modern applications for their high efficiency and ideally emission-free use, in contrast to currently more common fuels such as methane or natural gas that generate carbon dioxide. The only by-product of a hydrogen fuel cell is water vapour (Wikipedia Encyclopaedia Website).

The use of hydrogen for fuel cell applications represents one of the most environmentally sound methods for the production of electrical energy and is expected to gain wide usage in the near future for both automotive and small-to-medium scale stationary applications. Hydrogen productions have been carried out by several approaches, for example, steam reforming, electrochemical, photochemical, biological and thermochemical methods. Steam reforming is one of the least expensive hydrogen production methods at the present time. Roughly 97% of the worldwide hydrogen production is accomplished by steam reforming of natural gas and other fossil primary energy (Liguras et al., 2003).

There are many types of fuel cell. There are fuel cells of low and high temperature. There are aqueous FCs (such as alkaline or AFCs), direct methanol FCs (DMFCs), polymer electrolyte FCs (PEFCs), phosphoric acid FCs (PAFCs), molten carbonate FCs (MCFCs) solid oxide FCs (SOFCs) and proton exchange membrane fuel cells (PEMFC). For this research, the hydrogen produced will be fuelled for proton exchange membrane fuel cell (PEMFC) (Alcaide et al., 2006).

PEMFC are preferred for automotive applications, because their low operating temperature (around 80^{o}C) allow rapid startup; other potentially attractive features include relatively low projected cost and maintenance needs (Zalc et al., 2002). PEMFC are the most common type of fuel cells for light-duty transportation use, because they can vary their output quickly (such as for startup) and fit well with smaller applications. Primary advantages of PEMFC are that they react quickly to changes in electrical demand, will not leak or corrode, and use inexpensive manufacturing materials (plastic membrane) (KCC Energy Website).

1.2 Problem Statement

This work is dedicated to study on the hydrogen production plant from jet fuel for fuel cell application. There are two problem statement drawn for this research which are:

i. To identify potential design issues
ii. To obtain a preliminary estimate of the expected system efficiency

Identification of potential design issues basically involve carry out the simulation and obtain the important optimum value of parameters such as temperature, pressure and amount of feed for the hydrogen production plant. These also include other operating conditions that will makes the plant runs at optimum level. After that, a preliminary estimate of the expected system efficiency was determined. This is crucial for future development of this plant on the question of whether the plant is eligible to be realized for real applications.

1.3 Objectives and Scopes of Study

The objective of this study is to develop an optimized simulation model for hydrogen production plant from jet fuel for fuel cell applications. In order to achieve the objective, several scopes have been drawn:

1.3.1 Development of base case simulation

A steady state-state model of catalytic autothermal reforming process for a hydrogen production plant was developed by using Aspen HYSYS 2004.1. The autothermal process will consists of a few different processes which are total oxidation (TOX), partial oxidation (POX) process, steam reforming (SR) cracking, carbon dioxides reforming, carbon gasification and methanation. Conversion reactor was used for the autothermal reforming process

1.3.2 Base case model validation

The developed steady-state model results were compared with the mathematical stoichiometric calculation. This is to validate the theoretical reactions path with the actual simulation calculation inside the autothermal reactor.

1.3.3 Autothermal Reactor (ATR) Optimization

The objective of ATR optimization is to find out the best or optimum value of feed for air at 100 kgmole/h of kerosene or jet fuel. The optimum value would the one that give the best yield of hydrogen at a low yield of carbon monoxide. Temperature of the ATR reactor was also optimized. This was to find out at what temperature the ATR works best.

1.3.4 Heat Integration

The objective of this process is to apply the heat exchanger network. The heat was integrated to utilise every energy produces. This can in the end save the energy where by it had been used effectively.

1.3.5 Carbon Monoxide (CO) Clean Up

There are two subsystem that responsible to clean up the carbon monoxide produces in the ATR reactor before the effluents enters the Proton Exchange Membrane Fuel Cells (PEMFC). There are water gas shift (WGS) series of reactors and also preferential oxidation (PROX) reactor.

1.3.5.1 Water Gas Shift (WGS)

Water gas shift (WGS) series of reactors consist of high-temperature water gas shift (HTS), medium-temperature water gas shift (MTS) and low-temperature water gas shift (LTS). These series of reactor will take turn one after another to gradually decrease the composition of CO produced inside the ATR reactor. In these reactors WGS reaction took place therefore reduced the composition of CO where it will be converted into carbon dioxide (CO_2) and hydrogen (H_2).
Equilibrium type of reactors was used for the WGS processes.

1.3.5.2 Preferential Oxidation (PROX)

Preferential oxidation (PROX) reactor took place after the series of WGS reactors. In this reactor two PROX reactions that uses up the CO and hydrogen and converted them to carbon dioxide (CO_2) and water. These subsequently reduced the composition of CO before the ATR effluent enters the PEMFC. The effluent must contains less than 10 ppm of CO. Conversion reactor was used for the PROX reaction.

1.3.6 Plant Wide Optimization

In this scope it is aim to get the optimum value of water that should be fed into the ATR reactor and also the amount of air should be inject into the PROX reactor to assist the reduction of CO. In this case, it was divide into two section of where the optimization will takes place which are the WGS series of reactors and PROX reactor.

1.3.6.1 Water Gas Shift (WGS)

It is important to get the optimum value of water that should be fed in the ATR reactor as it will effect the reactions that occur inside the WGS reactors. The optimum value of water will ensure that CO will be converted in to CO_2 and H_2 and subsequently reduced its composition in the effluent.

1.3.6.2 Preferential Oxidation (PROX)

This is the last section of the building process where by after this the simulation would be complete for this research. In this part the PROX reactor is optimized to find out the best value of air should be inject into the PROX reactor. The optimum value of air will ensure the reduction of CO in the reactor's effluent before its enter the PEMFC.

1.4 Thesis Organization

This work is dedicated to construct a simulation of a jet fuel autothermal reformer for fuel cell applications and carried out to identify potential design issues and obtain a preliminary estimate of the expected system efficiency. The remainder of this paper is organized as follows; Chapter 2 gives out the literature review on the hydrogen production for fuel cell applications. In this section, researches done on the topic by other researchers were analyzed to gather information and knowledge.

The process of developing the plant was explored in Chapter 3 while in Chapter 4 process flow on how to build the plant was described. Results obtained and a discussion based on the results was carried out in Chapter 5 and finally, the conclusion and recommendations for future works are drawn in Chapter 6.

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