SIMULATION AND OPTIMIZATION OF DIESEL AUTOTHERMAL REFORMER FOR FUEL CELL APPLICATIONS

SITI NORHANUM BINTI FADLI

UNIVERSITI TEKNOLOGI MALAYSIA

ABSTRACT

Proton-electrolyte membrane (PEM) fuel cell systems offer a potential power source for utility and mobile applications. One of the most promising alternatives for large power requirements is to obtain the hydrogen from a liquid hydrocarbon fuel. A diesel fuel is an attractive option as feeds to fuel processor. Unfortunately, diesel fuel reforming is complicated and requires much higher temperatures. With the help of Aspen HYSYS 2004.1 the steady state model has been develop to optimize the performance, 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 optimized reaction composition, in terms of hydrogen production and carbon monoxide concentration, corresponds to A/F ratio of 45 and S/F ratio of 25. Under this condition, n-hexadecane conversion of 100%, H_2 yield of 19.8% on wet basis and carbon monoxide concentration of 25.428ppm can be achieved. The fuel processor efficiency is about 52.85% under these optimized conditions.

ABSTRAK

Sistem elektrolit polimer sel bahan api menawarkan sumber kuasa yang sangat berpotensi untuk kegunaan dan aplikasi pengangkutan. Salah satu alternatif untuk permintaan kuasa yang besar ialah untuk memperolehi hidrogen dari bahan api hidrokarbon. Diesel ialah pilihan yang menarik sebagai pembekal kepada bahan api yang diproses. Tetapi, penghasilan minyak diesel terlalu kompleks dan memerlukan suhu yang sangat tinggi. 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 dinamiknya. 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 45 dan 25 dimana penghasilan hidrogen dan kepekatan karbon monoksida adalah optimum. Di bawah keadaan ini, penukaran n-heksadekana adalah 100%, penghasilan hidrogen sebanyak 42% dan kepekatan karbon monoksida adalah 25.428 ppm. Di samping itu, kecekapan pemproses bahan api adalah 52.85% dalam keadaan optimum ini.

Dedicated to my beloved parents,
Fadli bin Saharuddin and Rohaya binti Said,
who have given me the most precious gift of all,
LIFE…

ACKNOWLEDGEMENTS

The core of research, besides having a good background of knowledge and a keen sense of curiosity, is about accepting successes and failures. The past few months of conducting this study have truly exposed me to obstacles that I believe, faced by every researchers out there. This dissertation is not just a product of my work alone, for many people have guided and supported me during the times when I needed them most.

My first appreciation definitely goes to my supervisor, Engr. Mohd. Kamaruddin bin Abd. Hamid who has always been there for me, guiding and supporting me all the way. Special thanks to my academic advisor, Pn. Zarina Bt. Ab Muis for giving me strengths and advices. My next appreciation goes to other seven of students who are under Engr. Mohd. Kamaruddin, by given full of cooperation's and supports.

I would not be here today without my beloved parents, who have always given me full support in every single thing I do and still are. Special thanks to my friend who have modeled me into a better person, for his never failing sense of optimism in me and light me up when I'm down, Ahmad Fairul Lizam.

CONTENTS

CHAPTER II LITERITURE REVIEW

CHAPTER III METHODOLOGY

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

(CEO_2 (HAS))	-	High surface area ceria
ΔH_{vap}	-	Latent heat of vaporation
Al_2O_3	-	Alumina
APU	-	auxiliary power units
ATR	-	Autothermal reforming
b.p.	-	Normal boiling point
C3	-	Organic compound
CH_4	-	Methane
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
C_p	-	Heat capacity
Cu	-	Cuprum
EOS	-	Equation of State
H_2	-	Hydrogen gases
H_2O	-	Water
LHV	-	Lower heating value
LPG	-	Propane/butane
MgO	-	Magnesium Oxide
MW	-	Molecular weight
Ni/SiO_2	-	Nikel/silicon dioxide
ODEs	-	Ordinary differential equations
OSR	-	Oxidative steam reforming
Pd	-	Palladium
PEM	-	Polymer-electrolyte membrane
POX	-	Partial oxidation

Pt	-	Platinum
SiO_2	-	Silicon (IV) dioxide
SMR-SE	-	Sorption enhance-steam methane reforming
SOFC	-	Solid oxide fuel cell
TiO_2	-	Titanium (IV) oxide
WETO	-	World Energy Technology and Climate Policy Outlook
ZrO_2	-	Zirconia

CHAPTER I

INTRODUCTION

1.1 Introduction

New drive systems with fuel cells and the energy carriers required could play a major part in improving the overall social environment. This is especially the case of improved conventional energy carriers and drive systems should reach to its limit then the new systems proposed offer a new quality of traffic in society. The worldwide demand for energy is growing more and more. The European “World Energy Technology and Climate Policy Outlook” (WETO) predict an average growth rate of 1.8% per year for the period 2000-2030 for primary energy worldwide. To ensure a competitive economic environment, energy system must meet the following societal needs at affordable prices:

i. Mitigate the effects of climate change;
ii. Reduce toxic pollutants;
iii. Plan for diminishing reserve of oil.

Measures should therefore be introduced which promote:

i. More efficient use of energy;
ii. Energy supply from a growing proportion of carbon-free sources;
iii. Transition technologies to reach the hydrogen quality

The on-board hydrogen production represents a valid alternative about safety, the stocked fuel is liquid and, moreover it can be supplied by the actual infrastructure. In this perspective, on-board hydrogen production has gained large important for fuel cell application, as vehicles power traction or auxiliary power units (APU) and it represents a good transition way to reach the aim of the hydrogen economy in mobile application (Cutillo *et al.,* 2006).

Polymer-electrolyte membrane (PEM) fuel cell systems offer a potential power sources for utility and mobile applications. Practical fuel cell systems use fuel processors for the production of hydrogen-rich gas. Diesel, as a liquid fuel is an attractive option as feed to a fuel processor. Diesel would be significantly less start-up cost of fueling vehicles than methanol. Diesel also has a much higher potential energy density than methanol (Amphlett, et al., 1998).

1.2 Problem Statement

This study is to develop the steady state model for simulation of hydrogen production using diesel as an input. The simulation of this model is demonstrated using Aspen HYSYS 2004.1. The amount of H_2 produced determines the efficiency of the fuel processor; the greater this amount, the higher is the fuel processor efficiencies. Thus, this study is planned to cover the following area:

1. What are the optimum Air-to-Fuel (A/F) and Steam-to-Fuel (S/F) molar ratios to get the high hydrogen production with CO concentration less than 10ppm?

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 than10ppm?

1.3 Objective 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 diesel via autothermal reforming. In order to achieve that objective, several scopes have been drawn:

1) Development of the base case simulation

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

2) Validation of the base case model

At this stage, the output from the simulation is 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 are used 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 reduced.

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 50ppm 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 used to investigate the influence of these parameters to hydrogen production, temperature and CO concentration.

6.2) PROX

The variations of air that is injected 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 diesel 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 diesel 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.

REFERENCES

Aartun, I. , Silberoza B. , Venvik, H. J. , Pfeifer, P. , Gorke, O. , Shcubert, K. , Holmen, A. (2005). "Hydrogen Production from Propane in Rh-impregrated Metallic Microchannel Reactors and Alumina Foams." *Catalysts Today, Volume* 105, *Issues* 3-4, 15 August 2005, pages 469-478

Amphlett, J. C. , Mann, R. F. , Peppley, B. A. , Roberge, P. R. , Rodrigues, A. , Salvador, J. P. (1998). "Simulation of a 250 kW Diesel Fuel Processor / PEM Fuel Cell System." *International Journal of Hydrogen Energy*. 71. 179-184

Avci, A. K. , Onsan, Z. I. , 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

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

Cheekatamarla, P. K. , Lane, A. M. (2005). "Efficient Bimetallic Catalysis for Hydrogen Generation from Diesel Fuel." *International Journal of Hydrogen Energy*. 30. 1277-1285

Chin, S. Y. , Chin, Y. H. , Amiridis, M. D. (2006). "Hydrogen Production via the Catalytic Cracking of Ethane over Ni/SiO_2 Catalysts." *Applied Catalysis A: General*. 300. 8-13

Dagaut, P. , 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

Erickson, P. A. (2004), "Hydrogen Production for Fuel Cells via Reforming Coal-derived Methanol." *Technical Report*. 823769. 100-116

Ersoz, A. , Olgun, H. , Ozdogan, S. (2005). "Reforming Options for Hydrogen Production from Fossil Fuel for PEM Fuel Cell." *Journal of Power Sources*. 1-7

Fernandez, E. O. , Rusten, H. K. , Jakobsen, H. A. , Ronning, M. , Holmen, A. , Chen, D. (2005). "Sorption Enhanced Hydrogen Production by Steam Methane Reforming Using Li_2ZrO_3 as Sorbent: Sorption Kinetics And Reactor Simulation." *Catalysis Today*. 106. 41-46

Koroneos, C. , Dompros, A. , Roumbas, G. , Moussiopoulos, N. (2005). "Advantages of the use of Hydrogen Fuel as Compared to Kerosene." *Resources, Conservation and Recycling*. 44. 99–113

Laosiripojana, N. , Assabumrungrat, S. (2005). "Hydrogen Production from Steam and Autothermal Reforming of LPG over High Surface Area Ceria." *Journal of Power sources*. 1-10

Ledjeff-Hey, K. , Kalk, T. , Mahlendorf, F. , Niemzig, O. , Trautmann, A. , Roes, J. (2000). "Portable PEFC Generator with Propane as Fuel." *Journal of Power Sources*. 86. 166-172

Liu, D.-J. , Kaun, T. D. , Liao, H. K. , Ahmed, S. (2003). "Characterization of Kilowatt-scale Autothermal Reformer for Production of Hydrogen from Heavy Metal." *International Journal of Hydrogen Energy*. 29. 1035-1046

Mariagiovanna (2005). “On-board Fuel Processor Modeling for Hydrogen-Enriched Gasoline Fuelled Engine.” *International Journal of Hydrogen Energy*. 1483-1490

Mizuno, T. , Matsumura, Y. , Nakalima, T. , Mishima, S. (2003), “Effect of Support on Catalytic Properties of Rh Catalysts for Steam Reforming of 2-propanol.” *Internacional Journal of Hydrogen Energy*. 28. 1393-1399

Mottons, L. V. , Noronha, F. B. (2005). “Hydrogen Production for Fuel Cell Application by Ethanol Partial Oxidation on Pt / CeO_2 Catalysis: The Effect of the Reaction Conditions and Reaction Mechanism.” *Journal of Catalysis*. 233. 453-463

Peters, R. , Dusterwald, H. G. , Hohlein, B. (2000). “Investigation of a Methanol Reformer Concept Considering the Particular Impact of Dynamics and Long-terms Stability for Use in a Fuel-cell-powered Passenger Car.” *Journal of Power Sources*.86. 507-517

Peters, R. , Dusterwald, H. G. , Hohlein, B. (2000). “Investigation of a Methanol Reformer Concept Considering the Particular Impact of dynamics and Long-terms Stability for Use in a Fuel-cell-powered Passenger Car.” *Journal of Power Sources*.86. 507-517

Sun, J. , Qiu, X.-P. , Wu, F. , Zhu, W.-T. (2005). “H_2 from Steam Reforming of Ethanol at Low Temperature over Ni / Y_2O_3, Ni / La_2O_3 and Ni / Al_2O_3 Catalysts for Fuel-Cell Application.” *International Journal of Hydrogen Energy*. 30. 437-445

Suzuku, T. , Iwanami, H.-I. , Yoshinari, T. (2000). “Steam Reforming of Kerosene on Ru/Al_2O_3 Catalyst to Yield Hydrogen.” *International Journal of Hydrogen Energy*. 25. 119±126

Wang, Y. H. , and Zhang, J. C. (2005). „ Hydrogen production Of Ni-Pd-Ce / γ-Al_2O_3 Catalyst by Partial Oxidation and Steam Reforming of Hydrocarbons for Potential Application in Fuel Cells." *Fuel.* 84. 1926-1932

Wang, Y. N. , Rodrigues, A. E. (2005). "Hydrogen Production From Steam Methane Reforming Coupled With In Situ CO_2 Capture: Conceptual Parametric study." *Fuel*. 84. 1778-1789

Wiese, W. , Emonths, B. , Peters, R. (1999). "Methanol Steam Reforming in a Fuel Cell Drive System." *Journal of Power Sources*.84. 187-193

Yanhui, W. , Diyong, Wu. (2001). "The Experimental Research for Production of Hydrogen from *n*-octane Through Partially Oxidation and Steam Reforming Method." *International Journal of Hydrogen Energy*. 26. 795-800

Yu, X. , Tu, S.-T. , Wang, Z. , Qi, Y. (2005). "On-board Hydrogen Production for Fuel Cells over Cu / ZnO/Al_2O_3 Catalyst Coating in a Micro-channel Reactor." *Journal of Power Sources*. 150. 57-66