SIMULATION AND OPTIMIZATION OF HYDROGEN PRODUCTION FROM AUTOTHERMAL REFORMING OF ETHANE FOR FUEL CELL APPLICATIONS

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Especially for my parents and friends

ACKNOWLEDGEMENTS

Thank to God for His kindness giving me a good health and full strength to finish this research. In time of difficulties, I believe He is always there to help and give me an internal encouragement.

First of all, I would like to thank my PSM Supervisor, Engr. Mohd. Kamaruddin Abd. Hamid, for giving us a guideline and idea for doing this research, and for the constant support and encouragement that he has shown to us from the beginning until the end of this research, especially when he contribute his time to teach us about the Aspen HYSYS simulation.

Fully thank to the management of control laboratory 2 for giving permission to us for using the computer in the lab, so that we can successfully finish our research.

I would like to thank to my colleagues Henry, Syafik, Badri, Azmil, Shahir and all that not mention for being helpful and supporting. Thank guys, I believe without your helps, this research will not be easier.

My biggest thank go to my family especially my father and mother, for their love, support and encouragement not only during my study in UTM but for my entire life. Nothing single word can express my love and gratitude for them.

Last but not least, to all my friends and those people who involved directly or indirectly to finish this research, thank you so much for your help.

ABSTRACT

Hydrogen fuel cell technologies have emerged as a promising future global energy. The technology called ‘hydrogen economy’ is a vision for future in with hydrogen replaced fossil fuels to reduce dependence on non-renewable energy and to cut down the environmentally harmful emissions. For this technology, hydrogen is mostly produced from hydrocarbons. Therefore, many researches have been conducted on hydrogen production from hydrocarbons to find the most economical, efficient and practical method of producing hydrogen for the fuel cell application. On this research we developed a simulation plant model using autothermal reforming reactor to produced hydrogen from ethane for fuel cell application. From the simulation plant model, we made an analysis on the behaviour of the process and determined the best condition of producing hydrogen from ethane. This research was carried out using computational tools, which is Aspen HYSYS 2004.1. Aspen HYSYS 2004.1 provides a simulation plant model of hydrogen production from ethane and allow us to study and analyze the process directly, by manipulating the process variable and unit operation topology. There are five steps to be follow in order to develop and analyze the simulation plant model, begin with base case development, base case validation, followed by ATR optimization, carbon monoxide clean up and finally the plant wide optimization. The results shown that optimum ratios of air/fuel and steam/fuel are 5.12 and 3.0, respectively to produce 40.26% hydrogen and CO less then 10 ppm with 82.07% fuel processor efficiency.

ABSTRAK

Teknologi sel bahan api hidrogen dibangunkan sebagai satu teknologi sumber tenaga global yang berpotensi untuk dimajukan pada masa hadapan. Teknologi yang dikenali sebagai 'ekonomi hidrogen' ini, diharapkan dapat menggantikan penggunaan minyak fossil untuk mengurangkan penggantungan kepada sumber tenaga yang tidak boleh diperbaharui disamping meenghapuskan pencemaran alam sekitar. Hidrogen bagi tujuan ini kebanyakannya dihasilkan daripada bahan-bahan hidrokarbon. Kajian terhadap penghasilan hidrogen daripada bahan hidrokarbon ini telah dijalankan untuk mencari kaedah yang paling ekonomik, berkesan dan praktikal dalam menghasilkan hidrogen untuk diaplikasikan pada sel bahan api hidrogen. Dalam kajian ini kami merangka model loji simulasi menggunakan '*autothermal*' reactor bagi penghasilan hidrogen daripada etana untuk aplikasi sel bahan api hidrogen. Daripada model ini, kami membuat analisis terhadap prestasi proses tersebut dan mencari keadaan terbaik untuk menghasilkan hidrogen daripada etana. Kajian ini dijalankan mengunakan program computer yang dikenali sebagai Aspen HYSYS 2004.1. Aspen HYSYS 2004.1 menyediakan model loji simulasi bagi penghasilan hidrogen daripada etana dan membenarkan kita membuat analisis secara langsung terhadap proses tersebut dengan memanipulasikan pembolehubah-pembolehubah proses dan unit operasinya. Terdapat lima langkah yang perlu diikuti dalam kajian ini iaitu perangkaan *'base case'*, pengesahan *'base case'*, pengoptimuman *ATR*, penyingkiran karbon monoksida dan akhir sekali pengoptimuman loji secara menyeluruh. Keputusan kajian menunjukkan dengan nisbah optimum udara/etana dan stim/etana ialah 5.12 dan 3.0, masing-masing, akan menghasilkan 40.26% hydrogen dan CO kurang daripada 10 ppm, dengan kecekapan *'fuel processor'* ialah 82.07%.

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NOMENCLATURE

c	-	heat capacity
F	-	flow rate
h	-	hour
h	-	height
M	-	mass
MW	-	molecule weight
N_{ss}	-	steady state degree of freedom
P	-	pressure
R	-	gas constant
P_c	-	critical pressure
ppm	-	parts per million
SV	-	space velocity
T	-	temperature
T_b	-	boiling point
T_c	-	critical temperature
V	-	volume
W	-	work
w	-	acentric factor
η	-	viscosity
$Ø$	-	fugacity coefficient
ρ	-	density
η	-	efficiency
n	-	molar flow rate

CHAPTER 1

INTRODUCTION

1.1 Introduction of Hydrogen

Hydrogen means "water creator", it was identified as a base material by Cavendish (1731-1810). At room temperature and under normal pressure, hydrogen is a colourless, odourless and non-poisonous gas which is lighter than air and helium. Hydrogen burns with a pale blue, almost invisible flame. At temperatures under -253 ºC hydrogen is in a liquid state (Bellona Report, 2002).

Hydrogen is the most common base material in the universe and is the main substance found in the sun and the stars. On earth practically all hydrogen is in a compound form with other elements. It reacts very readily with oxygen to create water. The water molecule consists of two hydrogen atoms and one oxygen atom. The oceans of the world therefore make up a huge storeroom of hydrogen. Hydrogen is also an important part of all organic matter. This includes vegetable, animal, and fossil matter. In the environment, hydrogen can be freely found in volcanic gasses, but its lightness allows it to escape beyond the earth's gravitational forces (Bellona Report, 2002).

1.2 Hydrogen Production

There are many ways of producing hydrogen. The following describes some of the most common techniques of producing hydrogen.

1.2.1 Gasification of Coal

Gasification of coal is the oldest method of producing hydrogen. In the old gas plants, the original gas piped in to cities was produced this way. This gas contained up to 60% hydrogen, but also large amounts of CO. Typically, the coal is heated up to 900ºC where it turns into a gaseous form and is then mixed with steam. It is then fed over a catalyst - usually nickel (Bellona Report, 2002).

1.2.2 Steam Reforming of Natural Gas

Steam reforming of natural gas is currently the cheapest way to produce hydrogen, and accounts for about half of the world's hydrogen production. Steam, at a temperature of 700-1000 ºC, is fed methane gas in a reactor with a catalyst, at 3-25 bar pressure. New methods are constantly being developed to increase the efficiency, and maximizing the heat process makes it possible to increase the utilization to over 85% and still make a profit (Bellona Report, 2002).

1.2.3 Autothermal Reforming of Oil and Natural Gas

Burning hydrocarbons with reduced amounts of oxygen is called partial oxidation. Autothermal reforming is a combination of partial oxidation and steam reforming. The term reflects the heat exchange between the endothermic steam reforming process and the exothermal partial oxidation (Bellona Report, 2002). The hydrocarbons react with a mixture of oxygen and steam in a "thermo reactor" with a catalyst.

Norsk Hydro's "Hydropower" concept, which is based on this process, uses air instead of pure oxygen in the reforming, both because of cost and because the nitrogen in the resulting feed gas has a lower burning temperature and reduced flame velocity. The feed gas can therefore be used in turbines developed for gas power plants

1.2.4 Electrolysis of Water

Water electrolysis is splitting water into hydrogen and oxygen. An electrolyser is a device for electrolysis. Water is subjected to electrical power and the result is hydrogen and oxygen (Bellona Report, 2002).

$$2H_2O + \text{energy} \rightarrow 2H_2 + O_2$$

This is the opposite reaction of what happens in a fuel cell. It is common to classify electrolysers according to the electrolyte it uses. Several cells are connected to achieve the desired capacity, just as with fuel cells. Some common electrolysers are as follows:

i) Alkaline electrolysers
ii) Polymer electrolyte membrane (PEM) electrolysers
iii) Steam electrolysers

1.2.5 Photoelectrolysis

The photovoltaic cell combines with a catalyst, which acts as an electrolyser and splits hydrogen and oxygen directly from the surface of the cell. This can quite realistically be a commercially viable means of producing hydrogen. The advantage with these systems is that they eliminate the cost of electrolysers and increase the systems' efficiency. Tests performed outdoors with silicon based cells have shown an efficiency of 7.8% in natural sunlight. Research is being done to increase the efficiency factor and the life span for such cells (Bellona Report, 2002).

1.2.6 Thermal Decomposition of Water

In a thermal solar power plant with a central collector such as Solar Two, a 10 MW power plant in California, the temperatures can reach over 3,000ºC. By heating water to over 2,000ºC, it is broken down into hydrogen and oxygen. This is considered to be an interesting and inexpensive method of producing hydrogen directly from solar energy. Research is also being done on the use of catalysts to reduce the temperature for dissociation. One central problem is the separation of gases at high temperatures to avoid recombining. The efficiency factor is uncertain (Bellona Report, 2002).

1.2.7 Gasification of Biomass

The amount of hydrogen in biomass is about 6-6.5 weight percent compared to almost 25% for natural gas. The processes involved in producing hydrogen from biomass resemble the processes in production from fossil fuel. Under high temperatures, the biomass breaks down to gas. The gas consists mainly of H_2, CO and CH_4 (methane). Steam is then introduced to reform CH_4 to H_2 and CO. CO is then put through the shift process to attain a higher level of hydrogen (Bellona Report, 2002).

1.2.8 Other Methods of Producing Hydrogen

There have more methods for producing hydrogen other than the methods that described above. Hydrogen also can be produce by Co-shift method, separation of CO_2, depositing, thermal dissociation, carbon black and hydrogen process, plasmatron and photobiological hydrogen production. There is further discussion surrounding new techniques which could be of consequence, as well as some interesting methods for producing hydrogen from renewable energy. Some of these are well-proven commercial techniques, while others, such as photobiological hydrogen production, are technologies under development (Bellona Report, 2002).

1.3 Application of Hydrogen

In early age, large quantities of hydrogen are needed in the chemical and petroleum industries, notably in the Haber process for the production of ammonia, which by mass ranks as the world's fifth most produced industrial compound. Hydrogen is used in the hydrogenation of fats and oils, and in the production of methanol. Hydrogen also is used in hydrodeakylation, hydrodesulfurization and hydrocracking. Other uses of hydrogen include rocket fuel, welding, producing hydrochloric acid, reducing metallic ores and filling ballon (Bellona Report, 2002).

Today, hydrogen not only produces for chemical and industries uses, but most importantly used in fuel cell as a fuel due to its potentially of non-polluting, inexhaustible, efficient, and cost attractive fuel for today's rising energy demands.

1.4 Problem Statement

This research is study on hydrogen production from ethane for fuel cell application. Hydrogen production via the autothermal reforming of ethane with the validated research done by Iwasaki et al.(2005).

It is important to study the design parameter for ethane fuel processor and to estimate the efficiency of the processor before it can be build in real plant. So to conduct this study, the optimized model of hydrogen production for fuel cells application using ethane as a raw material has been developed using Aspen HYSYS 2004.1 software.

1.5 Objectives and Scope of Study

The objective of this research is to simulate and optimized the hydrogen production plant from ethane for fuel cell application. In order to achieve the objective mentioned above, the following scopes have been drawn:

1) Base case model development
   Steady state model of hydrogen production from ethane was carried out using Aspen HYSYS 2004.1.

2) Base case model validation
   Steady state model was validated by comparing the calculated and simulated value of the molar flow components.

3) Autothermal reformer optimization

   Validated base case model of hydrogen plant was optimized by varies the molar flow of air.

4) Heat integration development

   Heat integration was developed by installing three heat exchanger to heating the raw materials that feed into the ATR reactor.

5) Carbon monoxide (CO) clean up

   Carbon monoxide clean up consist of two process which are the water gas shift process and the preferential oxidation process.

6) Plant wide optimization

   Plant wide optimization was developed by making an optimization on the water gas shift and preferential oxidation process.

1.6 Thesis Organization

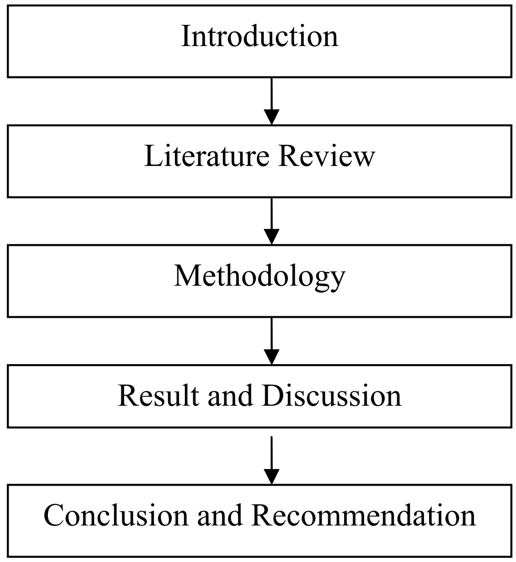

Figure 1.1: Thesis Organization

Figure 1.1 shows the organization of this thesis. This thesis starts with introduction of hydrogen production, literature review, methodology, result and discussion and finally the conclusion and recommendation. During the introduction, it describes generally about the method and resources to produce hydrogen. It also describes the problem statement and the objective and scope of this research. Literature review shows all the research that has been done on hydrogen production from hydrocarbon for fuel cell application.

In methodology, it shows the method or procedure that used for this research. It is important to have a correct methodology, because methodology will determine the result of the research. Result and discussion is all about the result, analysis and some discussion that performed on this research. Lastly the conclusion and recommendation are shows the summary for the whole research, conclusion that made base on result and some recommendation that useful for future study.

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