# SIMULATION AND OPTIMIZATION OF METHANOL AUTOTHERMAL REFORMER FOR FUEL CELL APPLICATIONS

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To my beloved parents and brother, for you’re supported and love.

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# ABSTRACT

The physically base study for steady state model for hydrogen production using autothermal reforming of methanol is developed using commercial simulator, Aspen HYSYS 2004.1. The development of the physical model will involve rigorous thermodynamics, and the data from mathematical stoichiometry calculation of total reaction hydrogen production from methanol as a steady state validation to build an accurate steady state model and reaction conversion is 100%. The initial steady state data will be generating in Aspen HYSYS 2004.1 that uses Autothermal Reforming (ATR), Water Gas Shift (WGS) and Preferential Oxidation (PrOx) reactor analysis. Validation results show that model developed using Aspen HYSYS 2004.1 is accurate and can be used for further analysis. Heat integration is implemented to utilize an excess heat generated by ATR. Here, all the inlet streams are heated up using that excess heat. Polymer Electrolyte Membrane Fuel Cell (PEMFC) can only tolerate carbon monoxide (CO) composition that is less than 10 ppm. Therefore, one of the objective of this study is to reduce the composition of CO that will satisfy the requirement of PEMFC, while optimize the hydrogen composition. In order to do that, the clean up process that consists of WGS and PrOx is implemented. After that, the plant wide optimization is carried out and the result show that the optimum conditions of 9.43 ppm of CO and 45.45% of hydrogen can be achieved with 1.5 and 0.6 ratio of Air to Fuel (A/F) and Steam to Fuel (S/F), respectively with fuel processor efficiency of 85.80%.

# ABSTRAK

Secara fizikal dan dasarnya, model yang berkeadaan malar dan mantap ini akan dibangunkan dengan menggunakan pensimulasi yang komersil iaitu Aspen HYSYS 2004.1. Pembangunan model fizikal ini akan melibatkan disiplin termodinamik dan juga data perkiraaan matematik yang seimbang daripada jumlah tindak balas penghasilan hidrogen daripada metanol dengan pemberlakuan dan pengesahan keadaan malar untuk membina sebuah model yang berkeadaan malar dan mantap di mana faktor pertukaran bagi tindak balas tersebut ialah 100%. Permulaan data model pada keadaan malar ini akan dijanakan dengan menggunakan Aspen HYSYS 2004.1 dengan menggunakan analisis reaktor autoterma menyusun semula (ATR), anjakan gas air (WGS) dan pengoksidaan keutamaan (PrOx). Keputusan pengesahan menunjukkan bahawa model yang dimajukan menggunakan Aspen HYSYS 2004.1 adalah tepat dan boleh digunakan untuk analisis lanjutan. Integrasi haba adalah pelaksanaan untuk menggunakan satu lebihan haba dijanakuasa oleh ATR. Di sini, semua aliran masuk komponen adalah dipanaskan dengan menggunakan haba lebihan. Polimer elektrolit membran bahan api sel (PEMFC) hanya boleh berfungsi apabila komposisi karbon monoksida (CO) kurang daripada 10 ppm. Oleh itu, salah satu daripada objektif kajian ini adalah untuk mengurangkan kandungan CO mengikut keperluan PEMFC, manakala mengoptimumkan komposisi hidrogen. Oleh sebab itu, proses pembersihan yang terdiri daripada WGS dan PrOx dilaksanakan. Selepas itu, hasil pengoptimuman menunjukkan bahawa syarat-syarat optimum 9.43 ppm bagi CO dan 45.45% hidrogen boleh dicapai dengan 1.5 dan 0.6 nisbah udara dengan bahan api (A/F) dan wap dengan bahan api (S/F), dengan kecekapan pemproses bahan api ialah 85.80%.

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# LIST OF SYMBOLS

| | | |
|---|---|---|
| ATR | - | Autothermal reforming |
| LTS | - | Low temperature shift |
| MTS | - | Medium temperature shift |
| ppm | - | Part per million |
| PrOx | - | Preferential Oxidation |
| PrOxR | - | Preferential oxidation reactor |
| WGS | - | Water gas shift |
| WGSR | - | Water gas shift reactor |
| $R$ | - | Gas constant |
| $T$ | - | Absolute temperature |
| $T_c$ | - | Critical temperature |
| $V$ | - | Molar volume of the pure solvent |
| $V_m$ | - | Volume of the pure solute |
| $a$ | - | Parameter describing attractive interactions between molecules |
| $b$ | - | Parameter describing volume exclusion and repulsive interactions |
| $k_{12}$ | - | Binary interaction parameter |
| $p_c$ | - | Critical pressure |
| $p_v(T)$ | - | Vapour pressure of the solute |
| $w$ | - | Centric factor |
| $x_2$ | - | Saturation of a solute of low volatility in a SCF |
| $1$ | - | Solvent |
| $2$ | - | Solute |
| $\eta$ | - | Efficiency |

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# CHAPTER I

# INTRODUCTION

## 1.1 Background Study

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. A 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 (Yacobucci et al., 2004).

The prospect of hydrogen becoming the main fuel for all energy-related applications, a “hydrogen economy,” and the continuing development of fuel cells to utilize hydrogen fuel has generated growing interest within the policy realm. This is especially true after two key initiatives by the Bush Administration the
Freedom CAR initiative to promote cooperative research and development between the federal government and the major American automakers on fuel cell vehicles;

and the President's Hydrogen Fuel Initiative to promote federal research and development on hydrogen fuel and non-automotive fuel cell technology (Yacobucci et al., 2004).

A fuel is any high energy substance that can be consumed to produce useful work. Examples include gasoline used to propel an automobile and coal used to generate electricity at a power plant. Hydrogen can also be used as a fuel, and is the most abundant element in the universe. However, hydrogen is not a primary fuel. That is, it does not occur naturally but instead is found most often as part of a larger molecule, such as water or petroleum. Today, most hydrogen is extracted by processing (reforming) methane (natural gas) at oil refineries and chemical plants. However, in the future hydrogen could potentially find widespread use as a fuel, either burned in combustion engines or combined with oxygen in fuel cells. Both methods produce useful energy either as motion or electricity, and both generate waste. To produce hydrogen fuel, two key components are necessary: energy and hydrogen atoms. In some cases, for example using natural gas, both components are supplied simultaneously as hydrogen atoms are separated from the methane molecule. In other cases, the two components are supplied separately. For example, electricity can be used to separate hydrogen from water to generate hydrogen fuel (Hydrogen, Fuel Cells and Infrastructure Technologies Program Website).

A fuel cell is an electrochemical device that uses hydrogen (or a hydrogen-rich fuel) and oxygen to produce electricity. It is physically and chemically similar to a battery, but as the name implies, fuel cells make use of an input fuel. They can be refuelled at any time, 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 (Yacobucci et al., 2004).

## 1.2 Problem Statement

It was desired to construct a simulation and optimization of a methanol autothermal reforming system to identify potential design issues and obtain a preliminary estimate of the expected system efficiency. Significant operating conditions could than be identified, and their effect on the overall system performance or efficiency could be evaluated.

## 1.3 Objective and Scopes of Study

The objective of this study is to develop and study an optimized steady state model of hydrogen production for fuel cell applications from methanol. In order to achieve that, several scopes has been planned. Scopes for this study are:

i. To develop steady state base case study model using simulation tool Aspen HYSYS 2004.1. Data from the calculation real reaction will be used in the simulation.
ii. To do validation between two data that is calculation data and simulation data from the base case study.
iii. To make optimization for inlet air into autothermal reactor (ATR) that produces the higher hydrogen molar flow.
iv. To do autothermal reactor (ATR) heat integration between three material streams that is methanol, air and water.
v. To do the clean up process for reduce carbon monoxide (CO) molar flow using water gas shift reaction (WGS) and preferential oxidation (PrOx) reaction.

vi. To make plant wide optimization for inlet water into water gas shift reactor (WGSR) and inlet air into preferential oxidation reactor (PrOxR) that will produce higher hydrogen molar flow.

## 1.4 Thesis Organization

The reminding of this thesis is organized such that each chapter addresses a specific part of the scopes outlined above. Chapter 2 describes in detail about hydrogen production for fuel cell application from several inputs and also from methanol. The methodology about development steady state model based on first principles using a commercial simulation package, Aspen HYSYS 2004.1 is described in chapter 3. In chapter 4, development of steady state model for hydrogen production plant from methanol for fuel cell application using a commercial software package, Aspen HYSYS 2004.1 is described in details. Results and discussion about all the scopes were explored in chapter 5. Lastly, the conclusion and recommendations were drawn in chapter 6.

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