การปรับปรุงสมรรถนะของระบบอิเล็กโทรไลซิสเซลล์แบบออกไซด์แข็งโดยร่วมกับการเผาไหม้บางส่วน

นายณัฐวุฒิ วิสิษฐดำรงค์กุล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

PERFORMANCE IMPROVEMENT OF SOLID OXIDE ELECTROLYSIS CELL SYSTEM INTEGRATED PARTIAL OXIDATION

Mr. Nuttawut Visitdumrongkul

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2014

Thesis Title	PERFORMANCE IMPROVEMENT OF SOLID OXIDE ELECTROLYSIS CELLSYSTEM INTEGRATED PARTIAL OXIDATION
By	Mr. Nuttawut Visitdumrongkul
Field of Study	Chemical Engineering
Thesis Advisor	Assistant Professor Amornchai Arpornwichanop, D.Eng.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering
(Professor Bundhit Eua-arporn, Ph.D.)

THESIS COMMITTEE
....Chairman
(Assistant Professor Apinan Soottitantawat, Ph.D.)
....Thesis Advisor
(Assistant Professor Amornchai Arpornwichanop, D.Eng.)
....Examiner
(Pimporn Ponpesh, Ph.D.)
....External Examiner
(Wisitsree Wiyarat, Ph.D.)

ณัฐวุฒิ วิสิษฐดำรงค์กุล : การปรับปรุงสมรรถนะของระบบอิเล็กโทรไลซิสเซลล์แบบออกไซด์แข็งโดยร่วมกับการเผาไหม้บางส่วน (PERFORMANCE IMPROVEMENT OF SOLID OXIDE ELECTROLYSIS CELLSYSTEM INTEGRATED PARTIAL OXIDATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. อมรชัย อาภรณ์วิชานพ, 114 หน้า.

อิเล็กโทรไลซิสเซลล์แบบออกไซด์แข็งเป็นเทคโนโลยีการผลิตไฮโดรเจนที่อาศัยหลักการของปฏิกิริยาทางไฟฟ้าเคมี เพื่อที่จะลดความต้องการของพลังงานไฟฟ้า พลังงานความร้อนจะสามารถถูกนำมาใช้ในระหว่างอิเล็กโทรไลซิสเซลล์แบบออกไซด์แข็งเพื่อช่วยในการแยกไอน้ำไปเป็นไฮโดรเจนและออกซิเจน โดยปฏิกิริยาการเผาไหม้บางส่วนเป็นปฏิกิริยาคายความร้อนที่สามารถผลิตพลังงานความร้อนในปริมาณมาก ดังนั้นกระบวนการอิเล็กโทรไลซิสเซลล์แบบออกไซด์แข็งโดยร่วมกับการเผาไหม้บางส่วนจะถูกนำมาช่วยในการปรับปรุงเพื่อให้กระบวนการผลิตพลังงานไฮโดรเจนมีประสิทธิภาพสูง ในงานวิจัยนี้การจำลองของกระบวนการร่วมกันระหว่างอิเล็กโทรไลซิสเซลล์แบบออกไซด์แข็งและการเผาไหม้บางส่วนจะถูกนำเสนอ นอกจากนั้นผลของตัวแปรในการดำเนินงานของกระบวนการเผาไหม้บางส่วน เช่น อัตราส่วนของออกซิเจนต่อคาร์บอน อุณหภูมิและความดันในการดำเนินงาน ที่ส่งผลต่อสมรรถนะของอิเล็กโทรไลซิสเซลล์แบบออกไซด์แข็งยังถูกศึกษาในงานนี้ โดยผลการจำลองพบว่า ประสิทธิภาพของอิเล็กโทรไลซิสเซลล์แบบออกไซด์แข็งสามารถถูกปรับปรุงจากเดิม 69.95 เปอร์เซ็นต์ ไปเป็น 84.97 เปอร์เซ็นต์ โดยการเผาไหม้บางส่วนถูกดำเนินงานที่อัตราส่วนของออกซิเจนต่อคาร์บอนเป็น 0.645 อุณหภูมิ 1373 เคลวิน และความดัน 5 บรรยากาศ นอกจากนั้นกระบวนนี้ยังถูกวิเคราะห์พลังงานและเอกเซอร์จี ซึ่งผลการวิเคราะห์พบว่า เตาปฏิกรณ์ของการเผาไหม้บางส่วนเป็นหน่วยที่เกิดการสูญเสียเอกเซอร์จีมากที่สุด

ภาควิชา วิศวกรรมเคมี
สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2557

ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5670202921 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: SOLID OXIDE ELECTROLYSIS CELL (SOEC) / SOEC SIMULATION / EXERGY ANALYSIS / PARTIAL OXIDATION REACTION

NUTTAWUT VISITDUMRONGKUL: PERFORMANCE IMPROVEMENT OF SOLID OXIDE ELECTROLYSIS CELLSYSTEM INTEGRATED PARTIAL OXIDATION. ADVISOR: ASST. PROF. AMORNCHAI ARPORNWICHANOP, D.Eng., 114 pp.

Solid oxide electrolysis cell (SOEC) is a hydrogen production technology based on an electrochemical principle. In order to reduce an electrical energy demand, a thermal energy can be applied to the SOEC for separating steam into hydrogen and oxygen. Partial oxidation reaction (POX) is an exothermic reaction that can produce high thermal energy. Thus, the SOEC integrated with the POX process would lead to an improved, high efficient process to produce hydrogen energy. In this study, modeling of the SOEC and POX integrated process is performed. Effect of operating parameters in the POX process, i.e., oxygen to carbon ratio, operating temperature and pressure, on the SOEC performance is studied. The simulation results show that the efficiency of the SOEC can be improved from 69.65% to 84.97% when it is integrated with the POX process run at the oxygen to carbon ratio of 0.645, temperature of 1373 K and pressure of 5 atm. Energy and exergy analyses of the proposed process are carried out with respect to changes in key operating parameters. The results indicate that the POX reactor is the unit having the highest exergy destruction.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
Academic Year:	2014		

ACKNOWLEDGEMENTS

The author would like to express my sincere appreciation to my thesis advisor, Assistant Professor Dr. Amornchai Arpornwichanop, who always introduces me in both research and education. Without his guidance and persistent help, this research would not have been possible.

In addition, the author is thankful to Mr. Chanon Mahisanan for giving advice in process modeling and Dr. Phanicha Tippawan for help on an exergy analysis.

The author would also like to especially thank the chairman, Assistant Professor Dr. Apinan Soottitantawat, and the other member of thesis committee, Dr. Pimporn Ponpesh and Dr. Wisitsree Wiyaratn, for their time and useful comments on this thesis.

Financial support by the Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University, the National Research University, Office of Higher Education Commission and the Thailand Research Fund is gratefully acknowledged.

Finally, the author is very grateful to his parents and friends in the Control and Systems Engineering Research Center for all their support throughout the period of this research.

CONTENTS

Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES

LIST OF FIGURES

LIST OF FIGURES

NOMENCLATURES

B_g	Permeability (m^2)
C_p	Heat capacity (kJ/mol K)
d_a	Thickness of anode (m)
d_c	Thickness of cathode (m)
$D_{H_2\text{-}H_2O}$	Molecular diffusion
$D_{H_2O}^{eff}$	Effective diffusion coefficient of steam (m^2/s)
$D_{H_2O,k}$	Knudsen diffusion,
E^0	Standard potential (V)
$E_{act,i}$	Activation energy at cathode and anode (J/mol K)
ex_{ch}	Specific chemical exergy (J/mole)
$ex_{ch,i}$	Standard chemical exergy of species of i (J/mole)
$\dot{E}x_d$	Exergy destruction (W)
ex_i	Specific exergy (J/mol)
ex_{ph}	Specific physical exergy (J/mole)
$\dot{E}x_Q$	Exergy of thermal energy (W)
$\dot{E}x_w$	Exergy of work (W)
F	Faraday’s constant
ΔG	Electrical demand (kJ/mol)
ΔG^0	Standard gibb free energy
h_i	Enthalpy of species of i at general state (J/mole)
$h_{i,0}$	Enthalpy of species of i at reference environment state (J/mole)
ΔH	Total energy demand (kJ/mol)
J	Current density (A/m^2)
$J_{0,a}$	Exchange current density at anode (A/m^2)
$J_{0,c}$	Exchange current density at cathode (A/m^2)
L	Thickness of electrolyte (m)
LHV_{in}	Low heating value of inlet (kJ/kmol)

NOMENCLATURES

LHV_{out}	Low heating value of outlet (kJ/kmol)
LHV_{H_2}	Low heating value of hydrogen (kJ/mol)
M_{H_2}	Molecular weight of hydrogen
M_{H_2O}	Molecular weight of steam
n_e	Number of electron for electrochemical reaction (2 electron)
n_p	Electrode porosity
N_{cell}	Number of cells
$\dot{N}_{CH_4\ in}$	Molar flow rate of fed methane
$\dot{N}_{H_{2,out}}$	Outlet molar flow rate of hydrogen (kmol/hr)
$\dot{N}_{H_2\ produced}$	Molar flow rate of produced hydrogen
$\dot{N}_{H_2O}$	Molar flow rate of steam (kmol/hr)
$\dot{N}_i$	Molar flow rate of species of i (mol/s)
$\dot{N}_{in}$	Molar flow rate of inlet (kmol/hr)
$\dot{N}_{out}$	Molar flow rate of outlet (kmol/hr)
P	Operating pressure of SOEC (atm)
p_{H_2}	Partial pressure of hydrogen (N/m^2)
p_{H_2O}	Partial pressure of steam (N/m^2)
p_i	Partial pressure of substance i (N/m^2)
p_{O_2}	Partial pressure of oxygen (N/m^2)
Q	Thermal energy of system (W)
Q_{cell}	Input thermal energy rate of SOEC (W)
Q_E	External Thermal energy for SOEC system
Q_{loss}	Energy losses (W)
Q_{out}	Heat rate of the reaction (kJ/hr)
Q_{ovp}	Heat of overpotential (W)
Q_r	Energy for the reaction in reactor (W)

NOMENCLATURES

Q_{swg}	Energy of sweep gas (W)
r	Average electrode pore radius (m)
R	Gas constant (8.314 J/mol K)
S_i	Entropy of species of i at general state (J/mole K)
$S_{i,0}$	Entropy of species of i at reference environment state (J/mole K)
T	Operating temperature (K)
T^*	Dimension less temperature
T_0	Reference temperature (298.15 K)
$T\Delta S$	Thermal demand (kJ/mol)
U_f	Utilization factor
W	Shaft work (W)
W_{comp}	Used energy for compressor (W)
W_{elec}	Power of SOEC (W).
W_{SG}	Used energy for steam generator (W)
y_i	Composition of species of i

Greek symbol

σ_{H_2}	Collision diameter of hydrogen (m)
σ_{H_2O}	Collision diameter of steam
α	Charge transfer coefficient
γ_i	Pre-exponential factor at cathode and anode, respectively (A/m^2)
$\frac{\varepsilon_{H_2}}{\kappa}$	Lennard-Jones Potentials of hydrogen
$\frac{\varepsilon_{H_2O}}{\kappa}$	Lennard-Jones Potentials of steam
$\eta_{act,a}$	Anode activation overpotential (V)
$\eta_{act,c}$	Cathode activation overpotential (V)
$\eta_{con,a}$	Anode concentration overpotential (V)
$\eta_{con,c}$	Cathode concentration overpotential (V)

NOMENCLATURES

η_{en}	SOEC energy efficiency
η_{ex}	Exergy efficiency
η_{ohm}	Ohmic overpotential (V)
μ	Dynamic viscosity (kg/ m s)
ν_i	Stoichiometric coefficients of substance
ξ	Electrode tortuosity
Ω_D	Dimensionless diffusion collision integral

CHAPTER I

INTRODUCTION

1.1 Importance and reasons

Presently, fossil fuels are used worldwide as the major energy source for power and heating generation. The combustion of these fossil fuels causes an emission of carbon dioxide, which is a greenhouse gas that contributes to the global warming problem (UNEP, 2012). For this reason, searching a clean alternative energy to replace fossil fuels becomes important. Hydrogen is regarded as an attractive, sustainable energy carrier. It is environmentally friendly as only steam is released as a by-product from the combustion process and has higher energy density than other fuels (e.g., methane, benzene and diesel) (Moriarty & Honnery, 2009). Hydrogen can be produced by various fuel processing technologies. Presently, steam reforming of natural gas is the most common method of hydrogen production (Angeli et al., 2014). Gasification is another thermo-chemical process that is widely used to convert carbonaceous materials into hydrogen, carbon monoxide and carbon dioxide (NREL, 2001). However, these hydrogen production technologies face environment issues caused by the emission of carbon dioxide. Alternatively, an electrolyser is emerged as a clean hydrogen technology because it can directly convert water to pure hydrogen and oxygen via an electrochemical reaction (Udagawa et al., 2007). Among the various types of electrolysis cells, the solid oxide electrolysis cell (SOEC) has been received considerable attention because it has high efficiency than other electrolysis cell types (Millet and Grigoriev, 2013). A SOEC is operated at high temperature around 800 to 1000 °C, which a thermal energy can be supplied from various heat sources, such as nuclear energy, geothermal energy or waste heat from other processes (Fujiwara et al., 2008). The high-temperature operation can improve kinetic energy for the electrochemical reaction and reduce the ion-transfer resistance in electrolyte layers, leading to an increased SOEC performance. In addition, it decreases the electrical requirement for the electrochemical reaction, causing a reduction in the operating cost. SOEC can be integrated with power plants or wind turbine for supplying electrical energy to it (Houcheng et al., 2013).

Most studies on SOECs for hydrogen production have presently relied on experiment. New electrode and electrolyte materials have been developed with high durability for high-temperature operation. Shao et al. (2013) optimized the electrolyte-support solid oxide electrolysis cell by a fabrication with dip-coating and co-sintering method. The pore ratio of Ni/YSZ was adjusted in this work. In addition, Zhang et al. (2013) tested a long-term durability of the SOEC stack made from advance material and novel treatment of interconnect for testing time of 1000 hours or more and operating temperature of 800 ºC. However, there are a few studies on modeling and simulation of SOEC. As modeling is an important tool for process analysis, design and optimization, a development of model to explain the SOEC behavior is important and interesting. Udagawa et al. (2007) investigated SOEC behavior and controled stack temperature by modeling. However, the modeling is quite difficult task, especially for complicated processes, which involve many parameters and variables. Use of well-developed flowsheet simulation software would facilitate performing a process simulation. This software generally contains various basic unit operation modules, such as reactor, separator and mixer, and thus, a design and development of new processes is simplified. In addition, the presence of rigorous thermodynamic and physical property database in the simulation program coupled with additional computational tool, e.g., calculator block, optimization and design specification, can assist designer for process improvement.

For performance analysis of SOEC, it is emphasizing on energy analysis because SOEC uses energy (electrical and thermal energy) for hydrogen production. Zhang et al. (2010) analyzed energy of electrolysis system by using three expressions of the system efficiency calculation. Recently, exergy analysis has been more interesting for evaluation of imperfection of process. Moreover, exergy analysis can assist to reach the goal for using energy resource more efficient (Hajjaji et al., 2012). However, energy and exergy will be analyzed simultaneously because these analyses use same principle calculation that is a thermodynamic method. Ni et al. (2007) investigated energy and exergy analysis of solid oxide steam electrolyzer plant to perform the effect of operating parameter on performance and efficiency of plant. Aforementioned, increasing of operating temperature is an important factor that can reduce electrical requirement and performance and efficiency of the system. Therefore, performance improvement of SOEC can be done by reduce electrical requirement of system.

To reduce the requirement of electrical energy for SOEC operation, use of thermal energy from external heat sources to supply to SOEC is an attraction solution. As SOEC can produce high purity hydrogen and oxygen, so the oxygen can be used as fuel for combustion to provide thermal energy used as external heat sources for SOEC in order to reduce electrical requirement. The methane combustion process includes complete combustion and partial combustion by using oxygen (Xu et.al., 2014). The complete combustion can produce steam and carbon dioxide which are not important. On the other hand, the partial oxidation can produce carbon monoxide and hydrogen, which hydrogen can be used as fuel in several processes. Generally, in the partial oxidation, air is used as fuel for combustion but the use of oxygen can reduce nitrogen oxide (NO_x) emission. Therefore, cooperation of SOEC with partial oxidation can enhance the ability of hydrogen production and reduce the electrical requirement because the thermal energy from partial oxidation can be used for SOEC.

This work will propose modeling of SOEC flowsheet by using Aspen Plus. A flowsheet simulation is used to evaluate the effects of parameter on the performance of SOEC. Then, SOEC will be integrated with partial oxidation process in order to supply thermal energy to SOEC for electrical requirement reduction. Methane is selected as a fuel for partial oxidation process. The amount of carbon dioxide produced from a new process will be compared with the conventional reforming process to demonstrate that the new process is low carbon dioxide emission. Finally, the exergy of process is analyzed to determine exergy destruction and efficiency in each unit.

1.2 Objectives

1. To simulate SOEC flowsheet and study effect of operating parameters on the performance of SOEC

2. To study effect of operating parameters of partial oxidation on performance of SOEC

3. To evaluate energy and exergy efficiency of process

4. To compare amount of carbon dioxide of this process with conventional reforming process

1.3 Scopes of work

1. SOEC system integrates with partial oxidation process by using existing function and unit operation of aspen plus software

2. Effect of operating parameters of SOEC, such as, operating temperature utilization factor and current density, on the performance of SOEC in term of electrical voltage used in SOEC.

3. Effect of operating parameters of partial oxidation is oxygen to fuel ratio and operating temperature and pressure on the performance of SOEC in term of electrical voltage used in SOEC.

4. Methane is used as a fuel for partial oxidation reaction

1.4 Dissertation overview

Chapter II reviews research that involve with SOEC modeling, partial oxidation simulation, energy and exergy analysis of SOEC and partial oxidation reaction.

Chapter III presents basic principle of electrical energy of SOEC calculation, partial oxidation reaction and exergy analysis method

Chapter IV describes procedure of simulation and validation result of SOEC and partial oxidation reaction.

Chapter V explains effects of SOEC operating parameter (i.e. operating temperature, current density, steam concentration, sweep gas type and number of cells) on SOEC performance and efficiency.

Chapter VI discusses effect of partial oxidation operating parameter (oxygen to carbon ratio, operating temperature and pressure) on SOEC and partial oxidation performance and efficiency. In addition, CO_2 emission of process in this dissertation with conventional reforming process is compared in this chapter.

Chapter VII analyzes exergy destruction of the process as well as effect of SOEC operating parameter on exergy destruction and efficiency of SOEC.

Chapter VIII is the last chapter which is conclusion and recommendation part for this dissertation.

CHAPTER II

LITERATURE REVIEWS

This chapter will present overview research that involve with this work. The chapter can be divided into three sections; SOEC modeling and system, partial oxidation process, and energy and exergy analysis. The SOEC modeling is importance because it can be used to predict performance and efficiency of SOEC. For the partial oxidation process is used to supply the thermal energy to SOEC for reduction of the SOEC electrical requirement. Finally, energy and exergy analysis are investigated to evaluate the efficiency of the process. Therefore, these topics must be reviewed in order to apply with this work discussed as below.

2.1 SOEC modeling and system

From Chapter 1 introduction, the environmental issue is a significant problem, as a result, SOEC have been received much attention in this time (UNEP, 2012). Therefore, there are SOEC researches studied configuration and modeling of SOEC by simulation method. In addition, it has also development of SOEC performance in order to reduce electrical energy requirement in SOEC (Ni et al., 2007; Udagawa et al., 2007; Udagawa et al. 2008).

The configurations of SOEC, there are cathode-supported, anode-supported and electrolyte-supported, each configuration can affect differently performance. Ni et al. (2007) studied the effect of configurations and parameters on performance of

SOEC. They found that the anode-supported was the best configuration design under same material property at operating temperature of 1273 K and steam molar fraction of 60 % because the limiting current density of cathode overpotential was very large that affect the ohmic overpotential. It became the main overall overpotential when current density was below limiting current density. For this reason, anode-support is chosen for configuration of SOEC in this work.

For the parameter of SOEC, there are many researches that studied parameter of SOEC. Ni et al. (2007) studied effect of electrode porosity, pore size, steam molar fraction and operating temperature. The result showed that increasing electrode porosity, pore size, steam molar fraction and operating temperature can increase the SOEC performance. Especially, the operating temperature was significant parameter that results to SOEC performance. Moreover, Udagawa et al. (2007) studied effect of temperature on SOEC performance. They confirmed that at high operating temperature (873-1273 K) can increase the SOEC performance. In addition, they also found that the SOEC can be operated either exothermic or endothermic operation. For this reason, in the next year, they studied stack temperature control with air flow rate that introduced to anode for SOEC thermal operation control. (Udagawa et al. 2008). The result found that increasing of air flow rate can control stack temperature for endothermic and exothermic operation.

Beside the steam electrolysis cell, there is a co-electrolysis cell which is an electrochemical device to convert steam and carbon dioxide mixture into hydrogen and carbon monoxide mixture or syngas. For the research of co-electrolysis cell, Ni (2012) developed electrochemical model to simulate the performance of co-electrolysis cell and compared with experimental data. The result shown that contribution of reversible water gas shift reaction for carbon monoxide production was depend on the operating temperature and inlet gas composition. Moreover, the simulation data is a good agreement with experimental data.

According to previous paragraph, the operating temperature is the most important parameter to control the performance of SOEC and co-electrolysis cell. Therefore, there are some researches that studied SOEC coupled with high thermal source such as nuclear reactor in order to enhance performance and efficiency of SOEC. Harvego et al. (2009) presented the coupling operation of high temperature electrolysis with advanced reactor (helium cooled reactor and supercritical carbon dioxide reactor) that was evaluated the effect of reactor outlet temperature on overall hydrogen production efficiency. This research demonstrated that increasing the reactor outlet temperature can enhance overall hydrogen production efficiency. Moreover, the coupling SOEC with high thermal source, use of methane which is introduced at anode to reduce electrical of SOEC, this approach can be called SOFEC. Frias et al. (2003) analyzed efficiency of SOFEC and compared with conventional SOEC. A SOFEC used electrical less than conventional SOEC, which SOFEC voltage was used below 1 volt.

However, SOEC must use electrical energy for producing hydrogen and oxygen production, as a result of high operating cost which is a disadvantage. For this problem, the SOEC system operated by electrical generate process can be solved this problem. Arashi et al. (1991) evaluated the efficiency of coupling of high temperature electrolysis cell with a solar cell for hydrogen production. The overall efficiency was estimated as 20-28 % which is twice of photo-voltaic combined with electrolysis cell. Houcheng et al. (2013) optimized the performance of high temperature electrolysis cell combined with solar concentrating beam splitting device system. The result showed that the maximum efficiency of system was depended on optimal current density. In addition, the ratio of distribute thermal and electrical energy was also important parameter for optimization this system.

In terms of experiment, Li et al. (2014) achieve high-efficiency hydrogen production using planar solid-oxide electrolysis stacks. They fabricate SOEC and test it under temperature of 800 ºC up to 500 hours without significant degradation. The SOEC can be achieved a maximum efficiency value of 52.7 % in 30 cell stack. Also, they can fabricate SOEC that can produce hydrogen at theoretical production rate. Department of Energy (DOE) in United States operated high temperature electrolysis cell (Stoots et al., 2008). They operated cell over 400 hour which can produce hydrogen at production rate of 0.9 Nm^3/h. For the cell temperature maintenance, SOEC was set in furnace which can produce temperature up to 1250 ºC. However, when SOEC was operated so long time, it always deteriorated. Zhang et al. (2014) evaluated durability of SOEC. They operated SOEC at 0.175 A/cm^2, 800 ºC which found that degradation rate of SOEC was 6.3 % $kh^{-1}$when it was operated over 200 hour. Moreover, SOEC was high degradation when it was operated at double of this operating current density.

The many researches involve simulation or optimization of SOEC which must use simulation tool in order to simulate and predict performance of SOEC, whether the Matlab, gPROMS Model Builder, C+ and FORTRAN language, these tools is used to calculate mathematic model. Ansys and Comsol is a simulation tool that used Computational Fluid Dynamic (CFD) method to simulate thermal and flow distribution. For example, Hawkes et al. (2005) created a model of planar SOEC by using a three-dimensional CFD and provided profiles of operating temperature, current density and hydrogen production over the range of operating condition. In addition to these tools, there are Aspen-Hysys and Unisim used to simulate the system. Nevertheless, the SOEC system was simulated by Aspen-Hysys or Unisim have a few studied, in contrast, the mathematic model have been popular to simulate SOEC system in this time.

Finally, the evaluation of SOEC system is an importance to provide the performance and efficiency of SOEC. Mingyi et al. (2008) studied thermodynamic analysis of SOEC efficiency. In this work, the thermodynamic analysis was an evaluation of the effect of electrical efficiency, thermal efficiency, electrolysis efficiency on the overall efficiency of system. The result found that at operating temperature of 1000 ºC, increasing of electrical, thermal and electrolysis efficiency can enhance overall efficiency from 33 % to 59 % as the maximum.

The literature review showed in the previous can be concluded that the operating temperature is an important parameter that is affected the performance of SOEC. So the thermal energy used in SOEC can be provided by various heat sources. Partial oxidation process is a one of external heat source that can be co-operated with SOEC which is explained in next topic.

2.2 Partial oxidation process simulation

The reforming process is a chemical process that can convert hydrocarbon compound to hydrogen and carbon monoxide mixture which can be called syngas. The partial oxidation is investigated in this work because this process is an exothermic process which can be used as thermal energy source of SOEC. In addition, this process can also use various fuels for occurrence the reaction (such as hydrocarbon or alcohol) because each fuel will provide different hydrogen production yield and thermal energy (Seo et al., 2002). Methane is the best choice for as a fuel of reforming process because of its abundance and inexpensive.

For partial oxidation process, oxygen to fuel ratio is an important parameter for operating temperature of the process, methane conversion and hydrogen production. Xu et al. (2014) studied effect of oxygen to fuel ratio and operating pressure on performance of the process. They varied oxygen to fuel ratio in range 0.6-0.7 and operating pressure of 1.2-6.0 MPa. The result found that increasing of oxygen to fuel ratio can enhance the operating temperature and methane conversion. Especially, at oxygen to fuel ratio range of 0.66-0.67 is optimal condition. Increasing of operating pressure can assist to increase methane conversion. Furthermore, the simulation of partial oxidation was studied by Khoshnoodi and Lim (1997). They simulated the process with gibb reactor module because this process is a multi-reaction system. For the sensitivity analysis, they analyzed by vary relative feed flow rates and reactor parameters to maximize the CO/O_2 yield as well as to minimize the undesired nitrogen compounds in the product stream. The optimum reactor temperature for maximizing the CO mole fraction in the synthesis gas was also calculated. Fernandes et al. (2006) optimized operating condition in partial oxidation reactor for reducing capital and operational costs. Controlling the H_2/CO ratio is an important factor for optimization. The result found that the optimal H_2/CO ratio should be around 0.7- 3 because the H_2/CO ratio is higher or lower than this ratio would require high temperature operation.

2.3 Energy and exergy analysis

The energy and exergy analysis have been increase interesting in this time. This analysis can assist to determine efficiency of energy and maximum theoretical useful work that can be obtained from an amount of energy, respectively (Hajjaji et al., 2012). Tsatsaronis (2007) revealed the definition and nomenclature of exergy analysis. This research presented the definition used for exergy analysis and discusses option of symbols. For the exergy analysis of SOEC, Ni et al. (2007) presented the energy and exergy analysis of SOEC plant. For the exergy analysis demonstrated that the SOEC has high exergy efficiency. The energy analysis showed that a heat exchanger was main caused for energy and exergy losses. Moreover, they also found that the difference between energy and exergy efficiency was a few at high operating temperature. However this research does not balance the energy of SOEC operation. In addition to Ni's research, Stempien et al. (2008) showed that exergy efficiency of SOEC has almost 80 % at operating temperature 1073 K and current density of 5000 A/m^2. The energy efficiency of SOEC is at 70 %.

In a part of reforming process, Smith et al. (2002) analyzed exergy of process and reaction pathway such as partial oxidation and combustion of methane. They found that the reactor where the large exergy loss is occurred and partial oxidation is lower exergy loss than combustion of methane reaction pathway. Hence, the reactor design is an important factor for process development. Moreover, Albrecht et al. (2002) studied exergy analysis of partial oxidation of natural gas reaction for gas turbine plant. The result of this research showed that the most exergy loss occurred on the partial oxidation reactor (9.57 %) and air separation unit (6.21 %). Bhattacharya et al. (2014) analyzed exergetic of gasification of biomass process for bio-hydrogen production. The reaction of gasification reactor was based on partial oxidation reaction. They reported that gasification reactor occur loss of exergy because it occurred irreversible chemical reactions. Therefore, many researches can be summarized that the major exergy loss in the process is occurred at partial oxidation reactor. Hence, process development will be emphasized on the partial oxidation reactor design.

CHAPTER III

THEORY

3.1 Principle of SOEC

A solid oxide electrolysis cell (SOEC) is a reverse process of a solid oxide fuel cell (SOFC) which is technology for hydrogen production via electrochemical reaction of steam at high temperature operation (Millet and Grigoriev, 2013). The SOEC structure consists of two solid structures that are electrolyte and electrode. The most popular electrolyte material is yttria-stabilized zirconia (YSZ) which is a ceramic material, it be durable to high temperature operation and good ion conductivity. The electrode is consists of cathode and anode. The cathode material is nickel-YSZ and the anode is lanthanum strontium manganite (LSM). A configuration of SOEC is planar and tubular. The planar configuration has received more attention because of low cost and good manufacturability as well as high durability at high pressure (Ni et al., 2008).

The principle of SOEC is shown in Figure 3.1. A steam is fed to cathode where the steam is reacted with electron in order to reduce into hydrogen and oxide ions. The hydrogen is moved out of cathode, whereas oxide ion is migrated through electrolyte to anode layer and then it is combined to oxygen molecules. The electrochemical reactions of SOEC are shown in equation (3.1) to (3.3).

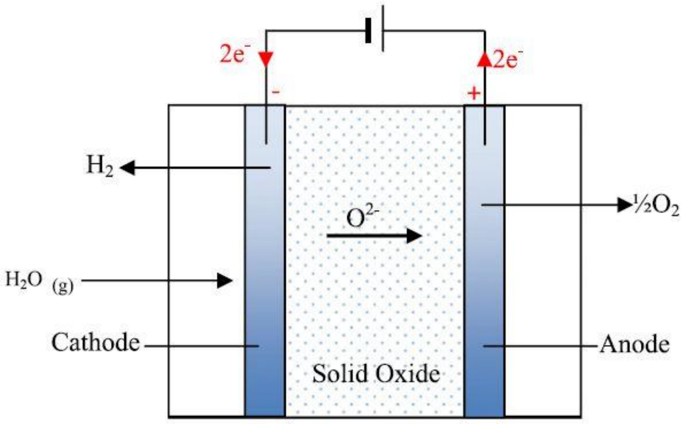

Figure 3.1 The principle of SOEC (Manage et al., 2011)

Cathode $H_2O + 2e^- \rightarrow H_2 + O^{2-}$ (3.1)

Anode $O^{2-} \rightarrow 0.5O_2 + 2e^-$ (3.2)

Overall reaction $H_2O \rightarrow H_2 + 0.5O_2$ (3.3)

The energy demand for occurred reaction consists of electrical and thermal energy due to the reaction of steam electrolysis is endothermic reaction, so the total energy demand can be calculated by equation (3.4) to (3.6) (Stempien et al. 2013). The operating temperature of SOEC is 800 to 1000 ºC which can assist to reduce electrical demand due to high thermal energy, showed in Figure 3.2. Moreover, it can also increase kinetic reaction without noble catalyst resulting to rate of reaction can be increased with low operating cost. However, the electrical and thermal energy demand must be optimized for the system.

$$\Delta H = \Delta G + T\Delta S \quad (3.4)$$

$$\Delta H = \Delta H^{\circ}_{298.15} + \int_{298.15}^{T} \Delta C_p dT \quad (3.5)$$

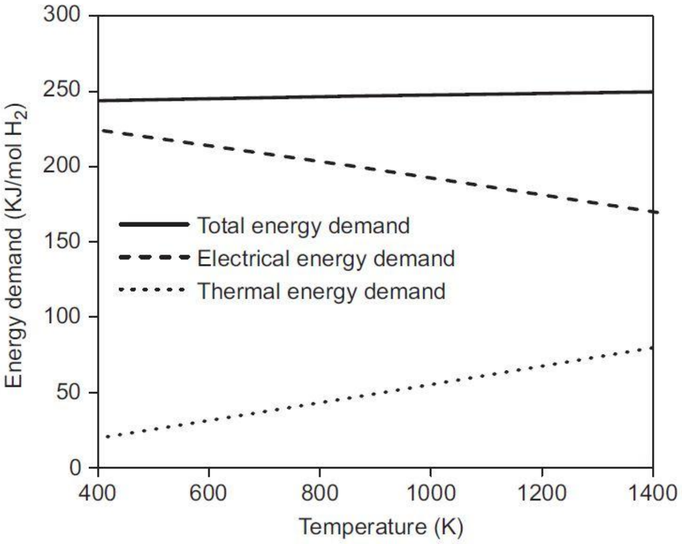

Figure 3.2 Effect of temperature on energy demand for SOEC (Ni et al., 2008)

$$\Delta S = \Delta S^{\circ}_{298.15} + \int_{298.15}^{T} \frac{\Delta C_{\mathrm{p}}}{T} dT \tag{3.6}$$

Where ΔH is the total energy demand (kJ/mol), ΔG is the electrical demand (kJ/mol) and $T\Delta S$ is the thermal demand (kJ/mol), C_p is the heat capacity (kJ/mol K)

3.2 Electrochemical model

3.2.1 Assumption of calculation

1. Steady state calculation
2. No heat loss and pressure drop
3. Ideal gas behavior
4. Zero dimension calculation
5. The model for calculation is based on model developed by Ni et al. (2007)

3.2.2 Equilibrium voltage calculation

The minimum work is required for electrochemical reaction take place called electrical work (W_{min}). It is a change of gibb free energy (ΔG) of the reaction, showed in equation (3.7). In addition, it also relate to cell voltage which can be called electromotive force or equilibrium voltage (E).

$$W_{\text{min}} = -\Delta G = n_{\text{e}} F E \tag{3.7}$$

Where n is the number of electron for electrochemical reaction (2 electron) and F is the Faraday’s constant (96487 C/mol)

The gibb free energy change of electrochemical reaction relate to activity coefficient. For gaseous case, it can be express in partial pressure term. Therefore, the gibb free energy change of steam electrolysis reaction can be calculated by equation (3.8).

$$\Delta G = \Delta G^0 + RT \ln\left(\frac{\prod P_{\text{products}}^{\upsilon_{\text{i}}}}{\prod P_{\text{reactants}}^{\upsilon_{\text{i}}}} \right) \tag{3.8}$$

Where ΔG^0 is the standard gibb free energy, R is the gas constant (8.314 J/mol K), T is the reaction temperature (K), p is the partial pressure of substance and υ_i is the stoichiometric coefficients of substance

Equation (3.8) must be substituted into equation (3.7) and then rearrange this equation to equation (3.9). This equation demonstrated that cell voltage depend on partial pressure of substance.

$$E = -\frac{\Delta G^0}{2F} - \frac{RT}{2F}\ln\left(\frac{\prod P_{\text{products}}^{\upsilon_i}}{\prod P_{\text{reactants}}^{\upsilon_i}}\right)$$

$$E = E^0 + \frac{RT}{2F}\ln\left(\frac{\prod P_{\text{reactants}}^{\upsilon_i}}{\prod P_{\text{products}}^{\upsilon_i}}\right) \tag{3.9}$$

Where E^0 is the standard potential (V)

From the steam electrolysis reaction (3.3), steam is used as reactant to produce hydrogen and oxygen. For this reason, equation (3.9) can be rearranged to equation (3.10) so called Nernst equation. This equation is used to calculate electrical demand of steam electrolysis reaction which depends on gas composition and temperature in SOEC. From the research of Ni et al., the standard potential is shown in equation (3.11) which depends on operating temperature of SOEC. However, the actual voltage of SOEC must higher than equilibrium voltage because the SOEC will occur irreversible losses.

$$E = E^0 + \frac{RT}{2F}\ln\left(\frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}}\right) \tag{3.10}$$

$$E^0 = 1.253 - 2.4516 \times 10^{-4} T \tag{3.11}$$

Where p_{H_2}, p_{O_2} and p_{H_2O} are the partial pressure of hydrogen, oxygen and steam (N/m^2), respectively

3.2.3 The actual voltage of SOEC

The actual voltage of SOEC will increase with increasing of current density, showed in Figure 3.3, because when current density is increased that result to occur irreversible losses. The irreversible losses can be called polarization, overpotential or overvoltage, it is mainly caused by activation overpotential at cathode and anode, ohmic overpotential and concentration overpotential at cathode and anode. Therefore, the actual voltage of SOEC can be calculated by equation (3.12).

$$V = E + \eta_{\text{conc,c}} + \eta_{\text{conc,a}} + \eta_{\text{act,c}} + \eta_{\text{act,a}} + \eta_{\text{ohmic}} \tag{3.12}$$

Where $\eta_{\text{conc,c}}, \eta_{\text{conc,a}}$ are the concentration overpotential at cathode and anode respectively (V), $\eta_{\text{act,c}}$, $\eta_{\text{act,a}}$ are the activation overpotential at cathode and anode respectively (V) and η_{ohmic} is the ohmic overpotential (V)

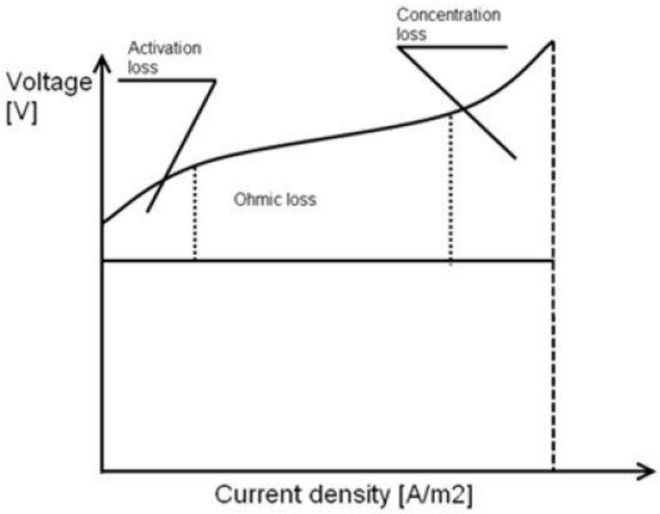

Figure 3.3 Effect of current density on voltage of SOEC (Stempien et al. 2013)

The activation overpotential is related to kinetic of electrochemical reaction. The voltage must high value in order to overcome activation energy of reaction. This overpotential occur during low current density both anode and cathode which can calculate by Butler-Volmer equation, showed in equation (3.13). However, this equation is quite complicate to calculation, for this reason, it can approximated and derived into hyperbolic sine form so called hyperbolic sin approximate equation showed in equation (3.14) (Noren and Hoffman, 2005).

$$J = J_0\left[\exp\left(\frac{\alpha 2F}{RT}\eta_{\mathrm{act}}\right) - \exp\left(-\frac{(1-\alpha)2F}{RT}\eta_{\mathrm{act}}\right)\right] \qquad (3.13)$$

$$\eta_{\mathrm{act,i}} = \frac{RT}{F}\sinh^{-1}\left(\frac{J}{2J_{0,i}}\right) \qquad (3.14)$$

Where α is the charge transfer coefficient, J is the current density (A/m^2) and $J_{0,\mathrm{i}}$ is the exchange current density at cathode and anode.

Moreover, the equation (3.14) can be derived into equation (3.15) which is a natural logarithm form equation. For the exchange current density can be calculated by equation (3.16) which it similarly with Arrhenius equation. Therefore, the exchange current density depends on operating temperature.

$$\eta_{\mathrm{act,i}} = \frac{RT}{F}\ln\left[\frac{J}{2J_{0,\mathrm{i}}} + \sqrt{\left(\frac{J}{2J_{0,\mathrm{i}}}\right)^2 + 1}\right] \quad (3.15)$$

$$J_{0,\mathrm{i}} = \gamma_{\mathrm{i}} \exp\left(-\frac{E_{\mathrm{act,i}}}{RT}\right) \quad (3.16)$$

Where γ_{i} is the pre-exponential factor of cathode and anode, respectively (A/m^2) and $E_{\mathrm{act,i}}$ is the activation energy of cathode and anode, (J/mol K)

The ohmic overpotential is caused by ion conductivity resistance of electrolyte which can be calculated by Ohm’s law, as a result, this overpotential is a linear function showed in equation (3.17). It depends on current density, thickness of electrolyte and operating temperature.

$$\eta_{\mathrm{ohm}} = 2.99\times10^{-5} JL \exp\left(\frac{10300}{T}\right) \quad (3.17)$$

Where L is the thickness of electrolyte (m)

The concentration overpotential or mass transport involved with resistance of the transport of reactant species approaching the TPB (at cathode) and the transport of product species leave out the TPB (at anode) which is performed by equation (3.18) and (3.19), respectively.

$$\eta_{\mathrm{conc,c}} = \frac{RT}{2F}\ln\left[\frac{\left(P_{\mathrm{H_2}} + JRTd_{\mathrm{c}} / 2FD_{\mathrm{H_2O}}^{\mathrm{eff}}\right)\cdot P_{\mathrm{H_2O}}}{\left(P_{\mathrm{H_2O}} - JRTd_{\mathrm{c}} / 2FD_{\mathrm{H_2O}}^{\mathrm{eff}}\right)\cdot P_{\mathrm{H_2}}}\right] \tag{3.18}$$

$$\eta_{\mathrm{conc,a}} = \frac{RT}{4F}\ln\left(\frac{\sqrt{\left(P_{\mathrm{O_2}}\right)^2 + \left(JRT\mu d_{\mathrm{a}} / 2FB_{\mathrm{g}}\right)}}{P_{\mathrm{O_2}}}\right) \tag{3.19}$$

Where d_c, d_a is the thickness of cathode and anode (m), respectively, $D_{\mathrm{H_2O}}^{\mathrm{eff}}$ is the effective diffusion coefficient of steam, μ is the dynamic viscosity (kg/ m s) and B_g is the flow permeability.

The cathode concentration overpotential is involved diffusion of reactant at cathode, for this reason, diffusion model need for the calculation. The Diffusion models are Fick’s model, Duty gas model and Stefan-Maxwell model, however, the most popular research use Fick’s model because it is non-complicate model and can describe the gas transport effectively. This model has effective diffusion coefficient of steam that can calculate by equation (3.20) (Ni et al., 2006). Moreover, it is a function of Knudsen Diffusion and Molecular Diffusion which can be calculated with kinetic theory and Chapman-Enskog theory performed by equation (3.21) and (3.22), respectively.

$$\frac{1}{D_{\mathrm{H_2O}}^{\mathrm{eff}}} = \frac{\xi}{n_{\mathrm{p}}}\left(\frac{1}{D_{\mathrm{H_2\text{-}H_2O}}} + \frac{1}{D_{\mathrm{H_2O,k}}}\right) \tag{3.20}$$

$$D_{\mathrm{H_2O,k}} = \frac{4}{3} r \sqrt{\frac{8RT}{\pi M_{\mathrm{H_2O}}}} \tag{3.21}$$

$$D_{\mathrm{H_2\text{-}H_2O}} = 0.00133\left(\frac{1}{M_{\mathrm{H_2}}}+\frac{1}{M_{\mathrm{H_2O}}}\right)^{1/2}\frac{T^{3/2}}{P\sigma^2_{\mathrm{H_2\text{-}H_2O}}\Omega_{\mathrm{D}}} \tag{3.22}$$

$$\sigma_{\mathrm{H_2\text{-}H_2O}} = \frac{\sigma_{\mathrm{H_2}}+\sigma_{\mathrm{H_2O}}}{2} \tag{3.23}$$

$$\mathit{\Omega}_{\mathrm{D}} = \frac{1.06036}{(T^*)^{0.1561}}+\frac{0.193}{\exp(0.47635T^*)}+\frac{1.03587}{\exp(1.52996T^*)}+\frac{1.76474}{\exp(3.89411T^*)} \tag{3.24}$$

$$T^* = \frac{\kappa T}{\varepsilon_{\mathrm{H_2\text{-}H_2O}}} \tag{3.25}$$

$$\frac{\varepsilon_{\mathrm{H_2\text{-}H_2O}}}{\kappa} = \sqrt{\frac{\varepsilon_{\mathrm{H_2}}}{\kappa}\cdot\frac{\varepsilon_{\mathrm{H_2O}}}{\kappa}} \tag{3.26}$$

Where ξ is the electrode tortuosity, n_{p} is the electrode porosity, $D_{\mathrm{H_2O,k}}$ is the Knudsen diffusion, $D_{\mathrm{H_2\text{-}H_2O}}$ is the molecular diffusion, r is the average electrode pore radius (m), $M_{\mathrm{H_2O}}$ and $M_{\mathrm{H_2}}$ are the molecular weight of steam and hydrogen, respectively, P is the operating pressure (atm), $\sigma_{\mathrm{H_2O}}$ and $\sigma_{\mathrm{H_2}}$ are the collision diameter of steam and hydrogen (m), $\mathit{\Omega}_{\mathrm{D}}$ is the dimensionless diffusion collision integral, T^* is the dimension less temperature and $\frac{\varepsilon_{\mathrm{H_2O}}}{\kappa}$ and $\frac{\varepsilon_{\mathrm{H_2}}}{\kappa}$ are the Lennard-Jones Potentials of steam and hydrogen, respectively (Reid et al., 1987)

The anode concentration overpotential is diffusion of oxygen as product at anode and it can be calculate with Darcy’s Law. This law is related to the permeability and dynamic viscosity can be calculated in equation (3.27) and (3.28), respectively (Todd and Young, 2002).

$$B_{\mathrm{g}} = \frac{\varepsilon^3}{72\xi(1-\varepsilon)^2}(2r)^2 \tag{3.27}$$

$$\mu = -1.692 + 889.75\tau - 892.79\tau^2 + 905.98\tau^3 - 598.36\tau^4 + 221.64\tau^5 - 34.75\tau^6 \tag{3.28}$$

$$\tau = \frac{T(K)}{1000} \tag{3.29}$$

Where B_g is the permeability (m^2) and μ is the dynamic viscosity (kg/m s)

SOEC electrical current can be calculated by using equation (3.30) which depends on number of electron transfer, steam utilization factor and mole flow rate of steam. This equation is a calculation of theoretical electrical current used at specified utilization factor. However, the electrical current is not used to calculate in electrochemical model, but as current density. Therefore, the current density can be calculated by equation (3.31). The power of SOEC is a significant parameter that represents the amount of electrical energy used for the reaction which is performed by equation (3.32).

$$I = \frac{n_{\mathrm{e}} \cdot U_{\mathrm{f}} \cdot F \cdot \dot{N}_{\mathrm{H_2O}}}{N_{\mathrm{cell}}} \tag{3.30}$$

$$Current\ density\ (J) = \frac{Electrical\ current\ (I)}{Area\ (A)} \tag{3.31}$$

$$W = I \cdot V \cdot N_{\mathrm{cell}} \tag{3.32}$$

Where U_{f} is the utilization factor, $\dot{N}_{\mathrm{H_2O}}$ is the mole flow rate of steam (kmol/hr), N_{cell} is number of cells and W is the electrical power (W)

The efficiency of SOEC can be calculated by equation (3.33) (Zhang et al., 2010). In addition, the occurred overpotentials in SOEC can be converted into thermal energy which can be used in the SOEC suddenly. The thermal energy which is generated by overpotentials can be called heat of overpotentials, determined by equation (3.34) (Ni et al., 2007).

$$\eta_{en} = \frac{\dot{N}_{\mathrm{H_{2,out}}} \cdot LHV_{\mathrm{H_2}}}{W + Q_{\mathrm{cell}}} \tag{3.33}$$

$$Q_{\mathrm{ovp}} = (\eta_{\mathrm{conc,c}} + \eta_{\mathrm{conc,a}} + \eta_{\mathrm{act,c}} + \eta_{\mathrm{act,a}} + \eta_{\mathrm{ohmic}}) \cdot J \cdot Area \cdot N_{\mathrm{cell}} \tag{3.34}$$

Where η_{en} is the SOEC efficiency, $\dot{N}_{\mathrm{H_{2,out}}}$ is the outlet flow rate of hydrogen , $LHV_{\mathrm{H_2}}$ is the low heating value of hydrogen, Q_{cell} is the thermal energy input rate of SOEC and Q_{ovp} is the heat of overpotential (W)

Utilization of heat of overpotentials can be separated into three cases. The first case, the heat of overpotentials is more than thermal demands for occurrence of reactions ($Q_{\mathrm{J}} > T\Delta S$), it make high stack temperature causing to operate in exothermic mode. The second case, the heat of overpotentials is less than thermal demand for occurrence of the reaction ($Q_{\mathrm{J}} < T\Delta S$) which results that SOEC is operated in endothermic mode. For the endothermic mode, the SOEC must use external heat energy to provide heat of system sufficiency for occurrence of the reaction. This external heat energy demand can be calculated by equation (3.35). Final case, the heat of overpotentials is equal to thermal demand for occurrence of the reaction

($Q_{\mathrm{J}} = T\Delta S$) that cause to thermo-neutral operation. This case is difficult to control and it is quite ideal case (Udagawa et al., 2007). Therefore, operation mode of SOEC will depend on the operating parameter such as stack temperature, current density, utilization factor and fed gas composition.

$$Q_{\mathrm{in,SOEC}} = \frac{J}{2F}\left[T\Delta S - Q_{\mathrm{J}}\right] \tag{3.35}$$

Where $Q_{\mathrm{in,SOEC}}$ is the external heat energy to supply in SOEC system

3.3 Methane reforming process for hydrogen production

Nowadays, the reforming process is a commercial technology for hydrogen production. For the fuel, methane is the most popular fuel that is used for reforming process due to its easily storage, inexpensive and abundance. There are three reforming technology which each technology has different of operating method, operating condition, advantage and disadvantage that is

Steam reforming process
Partial oxidation process
Autothermal reforming process

However, autothermal reforming process is not used in this work. Therefore, it is not discussed in this work. Steam methane reforming is a conventional process for hydrogen production plant. This process is used to compare amount of carbon dioxide emission with new process of this work. For the partial oxidation, it is an exothermic process which advantage of this process is it can supply heat to other process or SOEC system.

3.3.1 Steam methane reforming process

Steam methane reforming (SMR) is used on large scale industrial for hydrogen production which has carbon monoxide as by-product with hydrogen to carbon monoxide ratio of 3 to 1 respectively. Steam methane reforming proceeds in two steps, the reforming reaction of methane is highly endothermic reaction and water gas shift reaction is slightly exothermic reaction. These reactions are shown in equation (3.36) and (3.37) respectively.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{3.36}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3.37}$$

Generally, steam methane reforming is operated at temperature of 773-173 K, pressure of 20 bars and especially to steam to carbon ratio (S/C) of 2.2-3 for decreasing of coke formation (Naturwissenschaften, 2013). The advantage of steam methane reforming is highly hydrogen yield but some disadvantage of this process is requirement of external heat source because of its endothermic reaction (Wang and Rohr, 2002).

Presently, steam reforming can be used as commercial plant. For example, the Foster Wheeler Terrace-WallTM Reformer technology which is installed in Dubai is a steam reforming technology that can produce hydrogen 1.5 million Nm^3/day at hydrogen purity of 99.95 % and energy efficiency of plant of 89 %. (Spath and Mann, 2001) Therefore, this plant will be used to compare carbon dioxide emission with plant of this thesis.

3.3.2 Partial oxidation process

Partial oxidation of methane (POX) is a combustion reaction between methane and oxygen or air. This reaction can produce gases that compose of hydrogen, and carbon monoxide with ratio 2 to 1 respectively. This process is an exothermic reaction which is performed by equation (3.38) (Sayari, 2013). However, POX reaction is a complex reaction which can occur many side reactions (equation 3.39 to 3.42), shown as below (Xu et al., 2014).

$$\mathrm{CH_4 + 0.5O_2 \rightarrow CO + 2H_2} \tag{3.38}$$

$$\mathrm{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O} \tag{3.39}$$

$$\mathrm{CH_4 + 2H_2O \leftrightarrow CO + 3H_2} \tag{3.40}$$

$$\mathrm{CH_4 + CO_2 \leftrightarrow 2CO + 2H_2} \tag{3.41}$$

$$\mathrm{CO + H_2O \leftrightarrow CO_2 + H_2} \tag{3.42}$$

This process can be carried out either catalytic POX or non-catalytic POX. The catalyst that is added in the reaction can be reduced operating temperature. For the operating temperature range, the catalytic POX and non-catalytic POX will be operated at low temperatures (800-1000 ºC) and high temperatures (1000-1300 ºC), respectively.

The advantages of partial oxidation are fast reaction rate and start-up. Moreover, the process is exothermic process which does not require external heat source (Wang and Rohr, 2002). On the other hand, it can provide heat to other process. For the disadvantage of this process is hard to control of temperature because of coke and hot spot formation.

For the POX operation by using pure oxygen, it always feeds steam in order to reduce maximum temperature of flame within the reactor. This can help to protect the reactor. The suitable steam for using in the reactor is around 10 % volume of methane (Guo et al., 2012).

3.4 Exergy analysis

Exergy is the maximum theoretical useful work that can be produced when the control volume of system at general state (T, P) is brought to equilibrium at reference environment state (T_0, P_0) (Dincer and Rosen, 2013). However, the exergy will always loss. This loss can be divided in two different ways; exhaust and destruction, presented by Figure 4. The external losses or exhaust are caused by the exergy content in the matter streams that are not utilized such as purge stream or smoke, and cooling water. The internal losses or destruction are caused from irreversibility of the process such as reaction and heat transfer. Therefore, the exergy destruction is an important parameter to investigate the energy quality which can be determined by exergy balance equation, performed in equation (3.43).

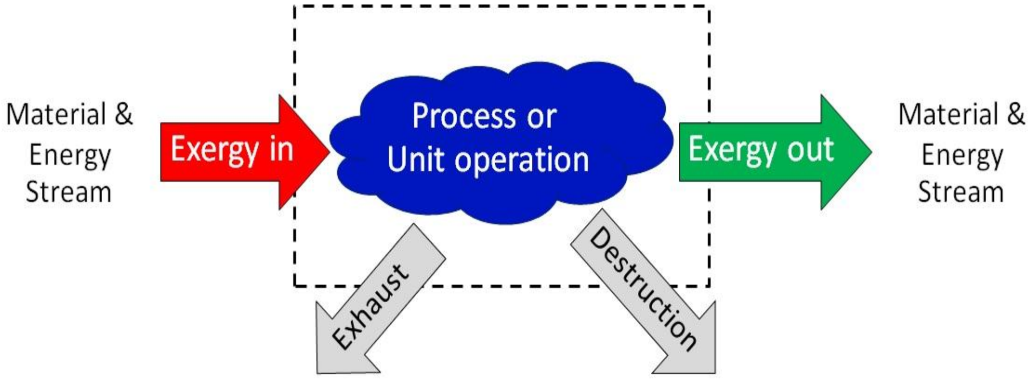

Figure 3.4 Exergy flow of process or unit operation (Gundersen, 2011)

$$\sum \dot{E}x_{\mathrm{Q}} + \sum_{\mathrm{in}} \dot{n}_{\mathrm{i}} ex_{\mathrm{i}} - \sum_{\mathrm{out}} \dot{n}_{\mathrm{i}} ex_{\mathrm{i}} + \dot{E}x_{\mathrm{w}} - \dot{E}x_{\mathrm{d}} = 0 \qquad (3.43)$$

Where $\dot{E}x_{\mathrm{Q}}$ is the exergy of thermal energy (W), $\dot{n}_i$ is the mole flow rate of species of i (mole/sec), ex_{i} is the specific exergy (J/mol), $\dot{E}x_{\mathrm{w}}$ is the exergy of work (W) and $\dot{E}x_{\mathrm{d}}$ is the exergy destruction (W)

The exergy of thermal energy is a thermal energy quality which is depended on temperature and heat of system, performed by equation (3.44) (Gundersen, 2011).

$$Ex_{\mathrm{Q}} = (1 - \frac{T_0}{T})Q \tag{3.44}$$

Where T_0 is the reference temperature (298.15 K), T is the temperature of system (K) and Q is the heat of system (W)

The specific exergy is a summation of specific physical exergy and specific chemical exergy which can be calculated by equation (3.45) (Ghannadzadeh et al., 2012)

$$ex_{\mathrm{i}} = ex_{\mathrm{ph}} + ex_{\mathrm{ch}} \tag{3.45}$$

Where ex_{ph} is the specific physical exergy (J/mole) and ex_{ch} is the specific chemical exergy (J/mole)

The specific physical exergy is the maximum useful work obtained by passing the stream of matter at the general state to the environmental state through physical processes. Such an exergy can be determined by equation (3.46).

$$ex_{\mathrm{ph,i}} = (h_{\mathrm{i}} - h_{\mathrm{i,0}}) - T_0(s_{\mathrm{i}} - s_{\mathrm{i,0}}) \tag{3.46}$$

Where h_{i} and $h_{\mathrm{i,0}}$ are the enthalpy of species of i at general state and reference environment state (J/mole), respectively, s_{i} and $s_{\mathrm{i,0}}$ are the entropy of species of i at general state and reference environment state (J/mole K), respectively

The specific chemical exergy is the maximum useful energy which would be attained by passing from the environmental state to the dead state, by means of chemical processes with reactants and products at the environmental temperature and pressure. Such an exergy can be determined by equation (3.46)

$$ex_{\mathrm{ch}} = \sum y_{\mathrm{i}} \cdot ex_{\mathrm{ch,i}} + RT_0 \sum y_{\mathrm{i}} \cdot \ln y_{\mathrm{i}} \tag{3.46}$$

Where y_{i} is the composition of species of i and $ex_{\mathrm{ch,i}}$ is the standard chemical exergy of species of i (J/mole)

The standard chemical exergy of each substance that is used in this work is presented in Table 3.1.

Table 3.1 Standard chemical exergy

Substance	**Chemical exergy (kJ/mol)**
H_2	236.09
H_2O (l)	0.90
H_2O (g)	9.50
O_2	3.97
CH_4	831.20
CO_2	19.48
CO	274.71
N_2	0.72

The exergy of work associated with shaft work done by the system. The shaft work includes all term of work (such as electrical work and mechanical work etc.) but excludes the work done by system with volume change, performed in equation (3.44) which exergy of work equals work that is used in each system.

$$\dot{E}x_{\mathrm{w}} = \dot{W} \tag{3.44}$$

Where $\dot{W}$ is the shaft work (W)

Finally, the efficiency of exergy for system can be calculated by equation (3.45). The exergy efficiency is defined by considering from matter inlet exergy and exergy destruction.

$$\eta_{\mathrm{ex}} = 1 - \frac{\dot{E}x_{\mathrm{d}}}{\dot{E}x_{\mathrm{in}}} \tag{3.45}$$

Where η_{ex} is the exergy efficiency

Exergy calculation will calculate exergy destruction of each unit operation of process in order to evaluate that which units that use useful work inefficiently. For the exergy destruction calculation, it can be calculated by using exergy balance equation. Exergy destruction calculated always is a positive value because exergy calculation is calculation for potential evaluation of energy that is used in each unit.

CHAPTER IV

MODELING AND VALIDATION

Simulation procedure of this work is shown in this chapter. The simulation topics of this work are SOEC, SOEC system and SOEC integrated with POX reaction simulation which each topic is presented as flowsheet by using Aspen Plus software. In addition, SOEC and POX is checked by comparing the predictive results with published experimental result in this chapter. The procedure of simulation in each topic is discussed as below.

4.1 SOEC simulation

In this thesis, SOEC is simulated by Aspen Plus software which is flowsheet simulator. SOEC flowsheet, showed in Figure 4.1, that uses existing unit operation modules (such as mixing, reactor and separation) and functions of software for simulation. The simulation approach of each module is explained in next section. For the italics term, it performs terminology of Aspen Plus.

4.1.1 Recirculation and mixing of reactant in MIXING block

SOEC use a steam as reactant for hydrogen production. In addition, hydrogen is also used as co-reactant in order to reduce partial pressure of steam in SOEC because use of steam as pure reactant will effect to high electrical energy for electrochemical reaction. For the simulation, the steam (Steam) is mixed with a part of product at *Mixer module* (named MIXING) because a part of product will contain hydrogen and steam that do not take place electrochemical reaction, so a part of product will be recycled for recirculation in cathode channel (Stream 7). A part of product will be separated by *FSplit module* (named SPLIT1) which provided split fraction by using design-spec function in order to provide steam to hydrogen ratio of stream 1.

4.1.2 Electrochemical reaction in CATHODE block

The electrochemical reaction of steam in SOEC occurs at cathode channel where hydrogen and oxygen (Stream 2) is produced. The cathode channel is simulated by *RStoic module* (named “CATHODE”) because this reaction is not reversible reaction. Therefore, this block is the best module for electrochemical reaction of steam. However, the reaction must use both electrical and thermal energy to carry out the reaction. Hence, the electrical energy used for the reaction can be calculated by using model from research of Ni et al. The electrical energy will be supplied to SOEC by stream POWER. For the thermal energy, it can be provided from external heat source (stream QE), heat of overpotential (stream QOVP) and anode channel (stream QA). In terms of simulation of “CATHODE” block, *RStoic block* temperature can be specified. Nevertheless, thermal energy for the reaction can be adjusted by design-spec function in order to balance overall energy of SOEC. For this reason, the design-spec function must specify external heat for the reaction as multiplied valuable.

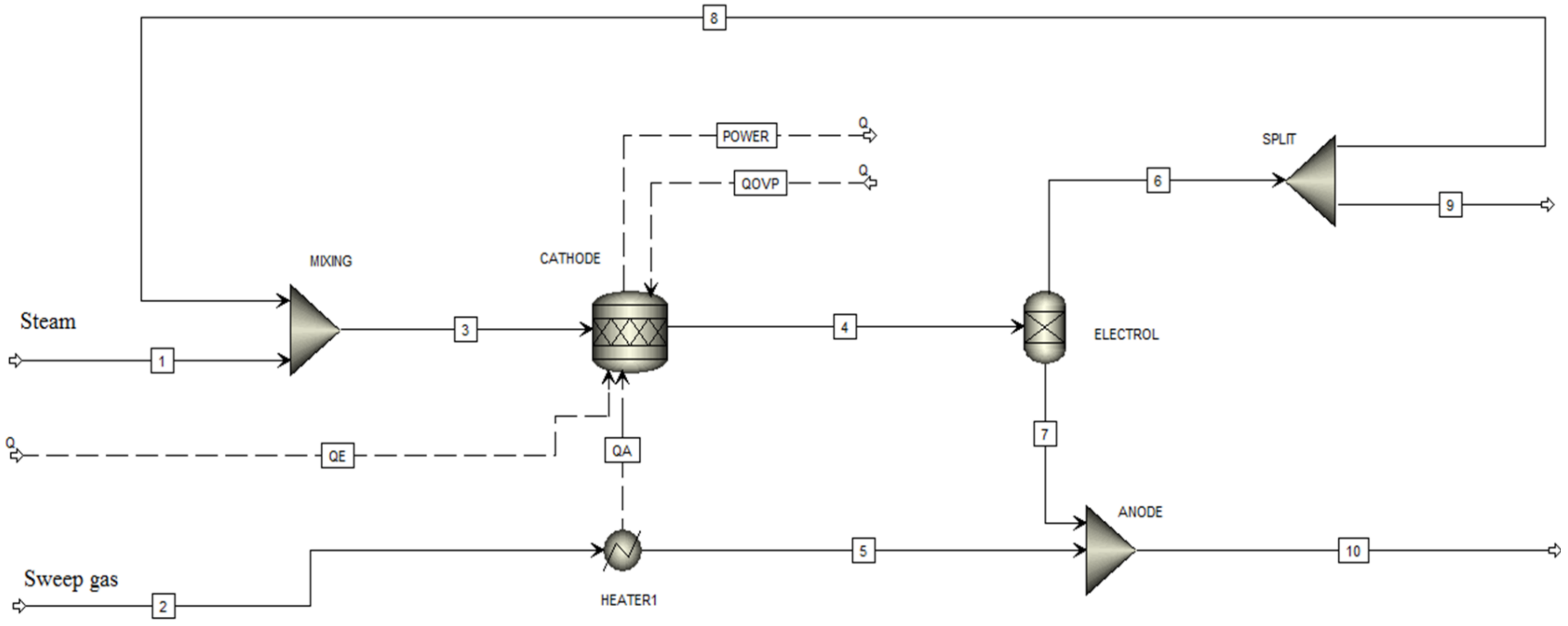

Figure 4.1 SOEC model flowsheet. Solid lines and dashed lines represent material streams and energy streams, respectvely

4.1.3 Hydrogen and oxygen separation in ELECTROL block

The hydrogen and oxygen produced by the reaction at cathode channel will be separated in electrolyte layer which is simulated by *Sep module* (named “ELECTROL”) in order to separate oxygen out of hydrogen and steam and then the oxygen will permeate to anode channel. For the ELECTROL block simulation, oxygen split fraction of *Sep module* is fixed as 1 in order to split only oxygen result to highly pure hydrogen at cathode channel.

4.1.4 Sweep gas in ANODE block

The oxygen produced at cathode channel will be sent to anode channel by passing of electrolyte layer. In the practice, the oxygen may be accumulated in anode channel. For this problem, sweep gas can be used to displace the oxygen out of anode channel. Moreover, sweep gas is also used as thermal carrier to transfer thermal energy each other between cathode and anode in order to balance the energy of SOEC. In the simulation, sweep gas (oxygen stream) is fed to *Heater module* (named “HEATER1”), which is set temperature equal to CATHODE block temperature by calculator block, in order to transfer thermal energy between CATHODE and HEATER1 block (Stream Q1). A second step is that sweep gas is mixed with oxygen which separated from ELECTROL block at *Mixer module* (named “ANODE”).

4.1.5 Cell voltage and overpotentials calculation

Electrical energy used for SOEC operation can be calculated from equation which is brought from Ni et al. research. The equations are expressed in Table 4.1 which is shown as below.

Table 4.1 Cell voltage and overpotential equation

Type equation	Equations	Eqn. No.
Equilibrium voltage	$E = E^0 + \frac{RT}{2F}\ln\left(\frac{P_{\mathrm{H_2}} \cdot P_{\mathrm{O_2}}^{1/2}}{P_{\mathrm{H_2O}}}\right)$	(3.10)
	$E^0 = 1.253 - 2.4516 \times 10^{-4} T$	(3.11)
Activation overpotential	$\eta_{\mathrm{act,i}} = \frac{RT}{F}\ln\left[\frac{J}{2J_{0,\mathrm{i}}} + \sqrt{\left(\frac{J}{2J_{0,\mathrm{i}}}\right)^2 + 1}\right]$	(3.15)
	$J_{0,\mathrm{i}} = \gamma_{\mathrm{i}} \exp\left(-\frac{E_{\mathrm{act,i}}}{RT}\right)$	(3.16)
Ohmic overpotential	$\eta_{\mathrm{ohm}} = 2.99 \times 10^{-5} JL \exp\left(\frac{10300}{T}\right)$	(3.17)
Concentration overpotential	$\eta_{\mathrm{conc,c}} = \frac{RT}{2F}\ln\left[\frac{\left(P_{\mathrm{H_2}} + JRTd_{\mathrm{c}} / 2FD_{\mathrm{H_2O}}^{\mathrm{eff}}\right) \cdot P_{\mathrm{H_2O}}}{\left(P_{\mathrm{H_2O}} - JRTd_{\mathrm{c}} / 2FD_{\mathrm{H_2O}}^{\mathrm{eff}}\right) \cdot P_{\mathrm{H_2}}}\right]$	(3.18)
	$\eta_{\mathrm{conc,a}} = \frac{RT}{4F}\ln\left(\frac{\sqrt{\left(P_{\mathrm{O_2}}\right)^2 + \left(JRT\mu d_{\mathrm{a}} / 2FB_{\mathrm{g}}\right)}}{P_{\mathrm{O_2}}}\right)$	(3.19)
Cell Voltage	$V = E + \eta_{\mathrm{conc,c}} + \eta_{\mathrm{conc,a}} + \eta_{\mathrm{act,c}} + \eta_{\mathrm{act,a}} + \eta_{\mathrm{ohmic}}$	(3.12)

In addition to cell voltage and overpotentials calculation, there are also other equations that are required for the operation and evaluation of SOEC. These equations are shown in Table 4.2

Table 4.2 Equation for SOEC operation and evaluation

Type equation	**Equation**	**Eqn. No.**
Utilization factor	$U_{\mathrm{f}} = \dfrac{J \cdot Area \cdot N_{\mathrm{cell}}}{n_{\mathrm{e}} \cdot F \cdot \dot{N}_{\mathrm{H_2O}}}$	(3.30)
Electrical Power	$W = J \cdot V \cdot Area \cdot N_{\mathrm{cell}}$	(3.32)
Heat of overpotential	$Q_{\mathrm{J}} = (\eta_{\mathrm{conc,c}} + \eta_{\mathrm{conc,a}} + \eta_{\mathrm{act,c}} + \eta_{\mathrm{act,a}} + \eta_{\mathrm{ohmic}}) \cdot J \cdot Area \cdot N_{\mathrm{cell}}$	(3.33)
SOEC efficiency	$\eta_{en} = \dfrac{\dot{N}_{\mathrm{H_{2,out}}} \cdot LHV_{\mathrm{H_2}}}{W + Q_{\mathrm{cell}}}$	(3.34)

4.1.6 Energy balance of SOEC

As electrical energy must be used in SOEC, it can be calculated by calculator block. In addition to electrical energy, SOEC must also use thermal energy to take place the reaction. Therefore, when electrical energy is reduced, thermal energy will be increased in order to balance energy of SOEC. This is why energy balance is required for simulation of SOEC. The net thermal energy for the SOEC operation can be calculated by equation (4.1) which is composed of heat for the reaction, heat of overpotential, heat of sweep gas and external heat. These thermal energies are used to take place the reaction and maintain cell temperature at a stable point because electrochemical reaction of steam is an endothermic reaction. Hence, energy balance equation for SOEC can be derived into equation (4.2). In the SOEC simulation, equation (4.2) can be assumed that amount of heat loss can be negligible. This is result that equation (4.2) can be derived into equation (4.3). Therefore, equation (4.3) is used for energy balance of SOEC.

$$Q_{\mathrm{T}} = Q_{\mathrm{r}} - Q_{\mathrm{ovp}} - Q_{\mathrm{swg}} - Q_{\mathrm{E}} \tag{4.1}$$

$$Q_{\mathrm{T}} - Q_{\mathrm{loss}} + W_{\mathrm{elec}} = 0 \tag{4.2}$$

$$Q_{\mathrm{T}} + W_{\mathrm{elec}} = 0 \tag{4.3}$$

Where Q_{r} is the energy for the reaction in reactor (W), Q_{ovp} is the heat of overpotential, Q_{swg} is the energy of sweep gas (W), Q_{E} is the external heat (W), Q_{loss} is the energy losses (W), and W_{elec} is the power of SOEC (W).

For the data in simulation and validation, they are shown in table 2 which are a data of Ni et al research. The anode configuration design is used for simulation because it is the best configuration for performance of SOEC.

Table 4.3 Input parameters and operating conditions

Parameters	**Values**
Operating Pressure, P (atm)	5
Pre-exponential factor for anode exchange current density, γ_a (A/m^2)	2.051×10^9
Pre-exponential factor for cathode exchange current density, γ_c (A/m^2)	1.344×10^{10}
Activation energy for anode, $E_{act,a}$ (J/mol)	1.2×10^5
Activation energy for cathode, $E_{act,c}$ (J/mol)	1.0×10^5
Current density (A/m^2)	2500
Electrode porosity, n_p	0.4
Electrode tortuosity, ξ	5.0
Average pore radius, r (μm)	0.5
Cell area, A (m^2)	0.04
Anode-support	
Electrolyte thickness, L (μm)	50
Cathode thickness, d_c (μm)	50
Anode thickness, d_a (μm)	500
Model for validation (momma et al.)	
Electrolyte-support	
Electrolyte thickness, L (μm)	1000
Cathode thickness, d_c (μm)	100
Anode thickness, d_a (μm)	100

4.1.7 SOEC validation

The result of SOEC validation between simulation and experimental data at different temperature is shown in Figure 4.2. The Momma et al. work is brought to use as experimental data for validation in this work. This experiment used steam to hydrogen ratio as 60 to 40. For the material of SOEC, the electrolyte, cathode, and anode layer is made from yttria stabilized zirconia (YSZ), nickel–YSZ (Ni–YSZ), and strontium-doped lanthanum-YSZ (LSM–YSZ), respectively. The thickness of each layer are 1000, 100 and 100 micrometers, respectively. The result show that it is good agreement between experimental and simulation data. However, SOEC modeling has limitation for calculation of hydrogen production rate in this time because SOEC uses both electrical and thermal energy which thermal energy cannot be measured (i.e. Ni et al. (2007), Udagawa et al. (2007) and Zhang et al. (2010)). For this reason, hydrogen production rate of SOEC must be calculated as theoretical hydrogen production rate which is calculated by basing on only electrical energy. This energy is used for utilization factor calculation by using equation (3.30). This equation calculates utilization factor of electrochemical reaction as number of electron that is used for production.

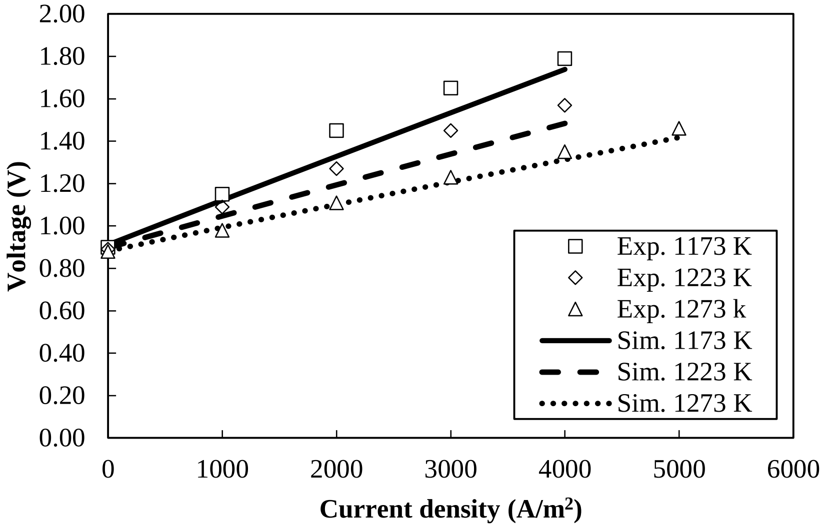

Figure 4.2 Validation of current density versus voltage between simulation and experimental data.at various operating temperature.

4.2 SOEC system

In order to analyze SOEC as real state, SOEC simulation as system should be required. This system is shown in Figure 4.4 which consists of steam generator, heat exchanger, compressor and SOEC. For heat that supply to SOEC is assumed that can transfer to SOEC perfectly. For the process description, it is described in topic 4.3 because topic 4.3 is SOEC system integrated with non-catalytic POX reaction which is main system of this work.

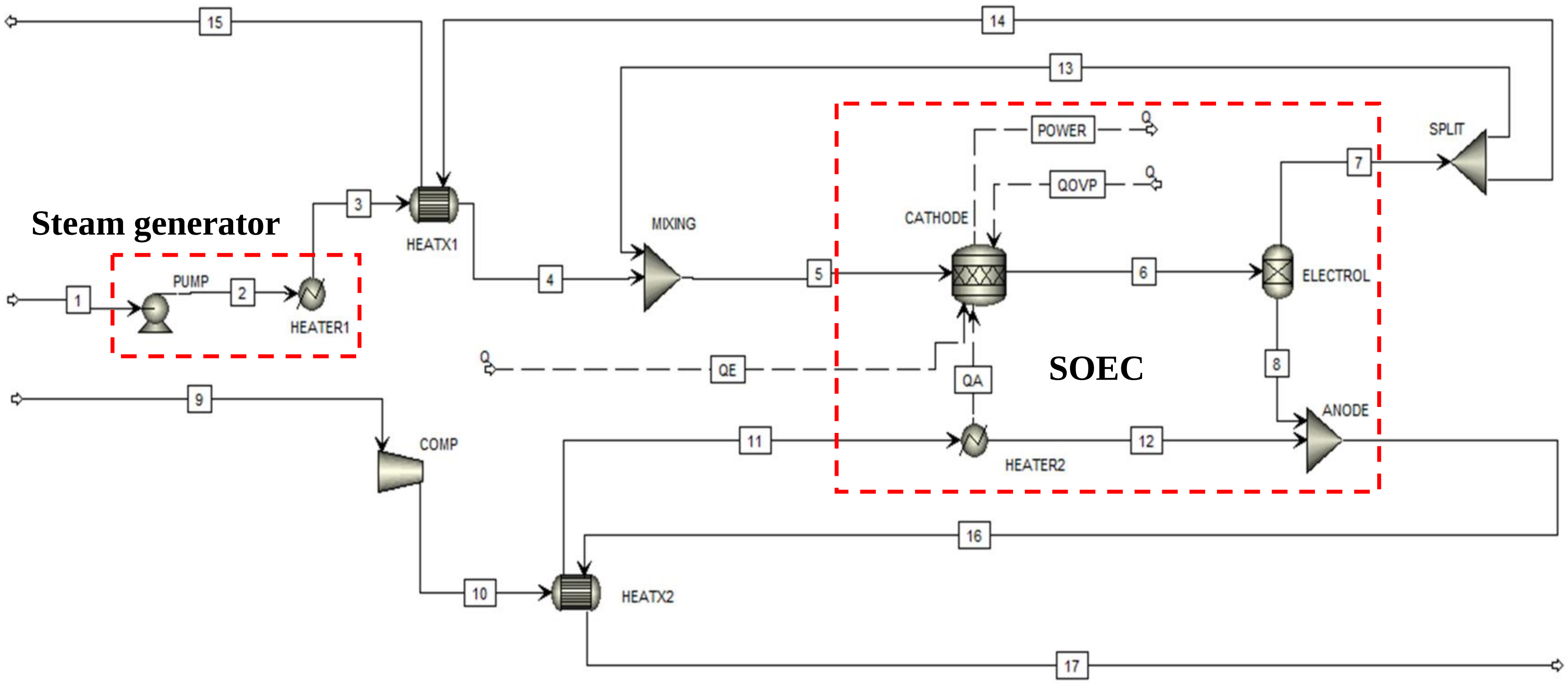

Figure 4.3 SOEC system flowsheet simulation

4.3 Non-catalytic partial oxidation simulation

A non-catalytic partial oxidation can be simulated in Aspen Plus software by using RGibbs reactor which shows in Figure 4.4. This reactor can calculate composition of reaction by using gibb free energy method which calculates phase equilibrium and chemical equilibrium because this reaction is complex reaction. In terms of the reaction, it is a reaction generating synthesis gas or syngas. In addition, this reaction is also used as commercial plant for syngas production in this time. For experimental data used for validation in this work, it is brought from patent of Texaco Development Corporation which produces synthesis gas by using direct partial oxidation of refinery gas with oxygen without catalyst. The stream composition and operating parameter of the patent are shown in Table 3. Moreover, this table performs simulation data that is used to compare with experimental data. The validation result of product stream (stream 3) between simulation and experimental data is shown in Table 3. This result is good agreement. Although hydrogen carbon monoxide and carbon dioxide are high accuracy, methane still high error. However, composition of methane is highly small when compare with hydrogen and carbon monoxide which are main product of POX reaction.

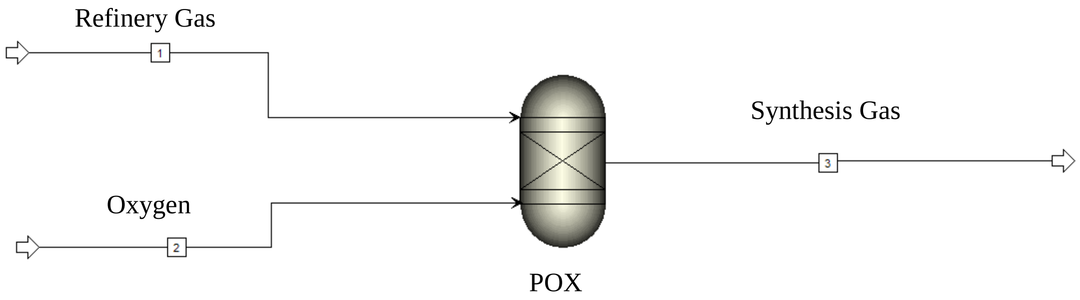

Figure 4.4 Partial oxidation flowsheet

Table 4.4 Operating parameters of non-catalytic partial oxidation and validation result (Reynolds et al., 1973)

	Stream 1 (Refinery gas)	**Stream 2 (Oxygen)**	**Stream 3 (Synthesis gas)**	
			Simulation	**Experiment**
Composition (%)				
Methane	95.8	0	0.0374	0.4
Ethane	2.6	0	1.774×10^{-7}	0
Propane	0.4	0	2.153×10^{-12}	0
Butane	0.8	0	2.708×10^{-17}	0
Carbon dioxide	0.3	0	1.446	1.5
Nitrogen	0.6	0	0.196	0.3
Oxygen	0	100	2.879×10^{-11}	0
Water	0	0	8.700	9.1
Hydrogen	0	0	57.278	56.4
Carbon monoxide	0	0	32.342	32.3
Operating parameter				
Temperature (F)	1000	300	2600	2600
Pressure (psig)	500	500	450	450
Flow rate (mol/hr)	616	413	1888.476	1879
Operating parameter of RGibb reactor				
Temperature (K)	2600			
Pressure (psig)	450			

In terms of POX reaction efficiency and hydrogen yield, they can be calculated by using equation (4.4) and (4.5), respectively. These efficiency and hydrogen yield are performance index of the reaction

$$\eta_{\mathrm{en}} = \frac{\dot{N}_{\mathrm{out}} \cdot LHV_{\mathrm{out}} + Q_{\mathrm{out}}}{\dot{N}_{\mathrm{in}} \cdot LHV_{\mathrm{in}}} \tag{4.4}$$

$$\mathrm{H_2\ yield} = \frac{n_{\mathrm{H_2\ out}}}{n_{\mathrm{CH_4\ in}}} \tag{4.5}$$

Where $\dot{N}_{\mathrm{out}}$ and $\dot{N}_{\mathrm{in}}$ are the molar flow rate of outlet and inlet (kmol/hr), respectively, Q_{out} is the heat flow rate of the reaction (kJ/hr) and LHV_{out} and LHV_{in} are the low heating value of outlet and inlet (kJ/kmol)), respectively. $n_{\mathrm{H_2\ out}}$ and $n_{\mathrm{CH_4\ in}}$ are molar flow rate of hydrogen produced and methane fed, respectively.

4.4 SOEC integrated with non-catalytic partial oxidation

The SOEC can increase performance by integrating with non-catalytic POX reaction as discussed. In generally, SOEC is heated for control temperature by taking it into furnace. For this reason, this process can be done by taking SOEC in non-catalytic POX reactor which has many assumptions for this process that are listed as below. In term of POX reaction efficiency, it can be calculated by using equation (4.4). This efficiency is performance index of the reaction.

Assumption for this process

1. Steady state calculation
2. No heat losses
3. No pressure drop within POX reactor
4. Thermal energy from POX reaction can be transferred to SOEC perfectly
5. Zero-dimension calculation

The process flowsheet which is shown in Figure 3.5 consists of several main units operations which are steam generator, heat exchanger, compressor, SOEC and partial oxidation reactor.

For the procedure of this system, firstly, water is fed to steam generator which is used to produce steam for using as reactant in SOEC. Then, the generated steam is separated into 2 streams. One stream is used in POX reaction and the other is moved pass heat exchanger 1 to increase temperature for preparing for operation of SOEC by heat exchange with product from cathode channel. Next, the steam must be mixed with some of product from cathode for adjusting steam to hydrogen ratio at Mixing. The steam is already fed to cathode of SOEC. In terms of oxygen for feeding into anode channel, oxygen at standard state must be increased pressure at compressor 1. Then, the oxygen must be exchanged heat with anode product at heat exchanger 2 and feed oxygen to the anode channel of SOEC. When the SOEC carries out the reaction, hydrogen and steam is produced at cathode channel, but oxygen is produced at anode channel. The hydrogen and steam is split into 2 streams. One stream is used to adjust steam to hydrogen ratio and the other is reduced temperature by heat exchanging with steam from steam generator. For the produced oxygen at outlet of anode channel, it is reduced temperature by heat exchanging with oxygen and then it is reduced temperature again at heat exchanger 3 by heat exchanging with methane which is used as reactant for POX reaction. The oxygen that is reduced temperature is split into 2 streams. One stream is used in POX reaction, the other is sent to exit. The methane, oxygen and steam from steam generator are pressurized at compressor 2 for preparing for POX reaction operation at POX reactor. Thereafter, the pressurized stream is fed to POX reactor where POX reaction is taken place. Finally, the product of POX reaction is sent out of the reactor.

For calculation of SOEC-POX system efficiency which is used as performance index of this system, it can be calculated by using equation (4.6).

$$\eta_{\mathrm{en}} = \frac{(\dot{N}_{\mathrm{H_{2,out}}} \cdot LHV_{\mathrm{H_2}})_{\mathrm{SOEC}} + (\dot{N}_{\mathrm{out}} \cdot LHV_{\mathrm{out}})_{\mathrm{POX}}}{W_{\mathrm{SOEC}} + W_{\mathrm{SG}} + W_{\mathrm{comp}} + (\dot{N}_{\mathrm{in}} \cdot LHV_{\mathrm{in}})_{\mathrm{POX}}} \tag{4.6}$$

Where W_{SG} and W_{comp} are used energy for steam generator and both compressors, respectively.

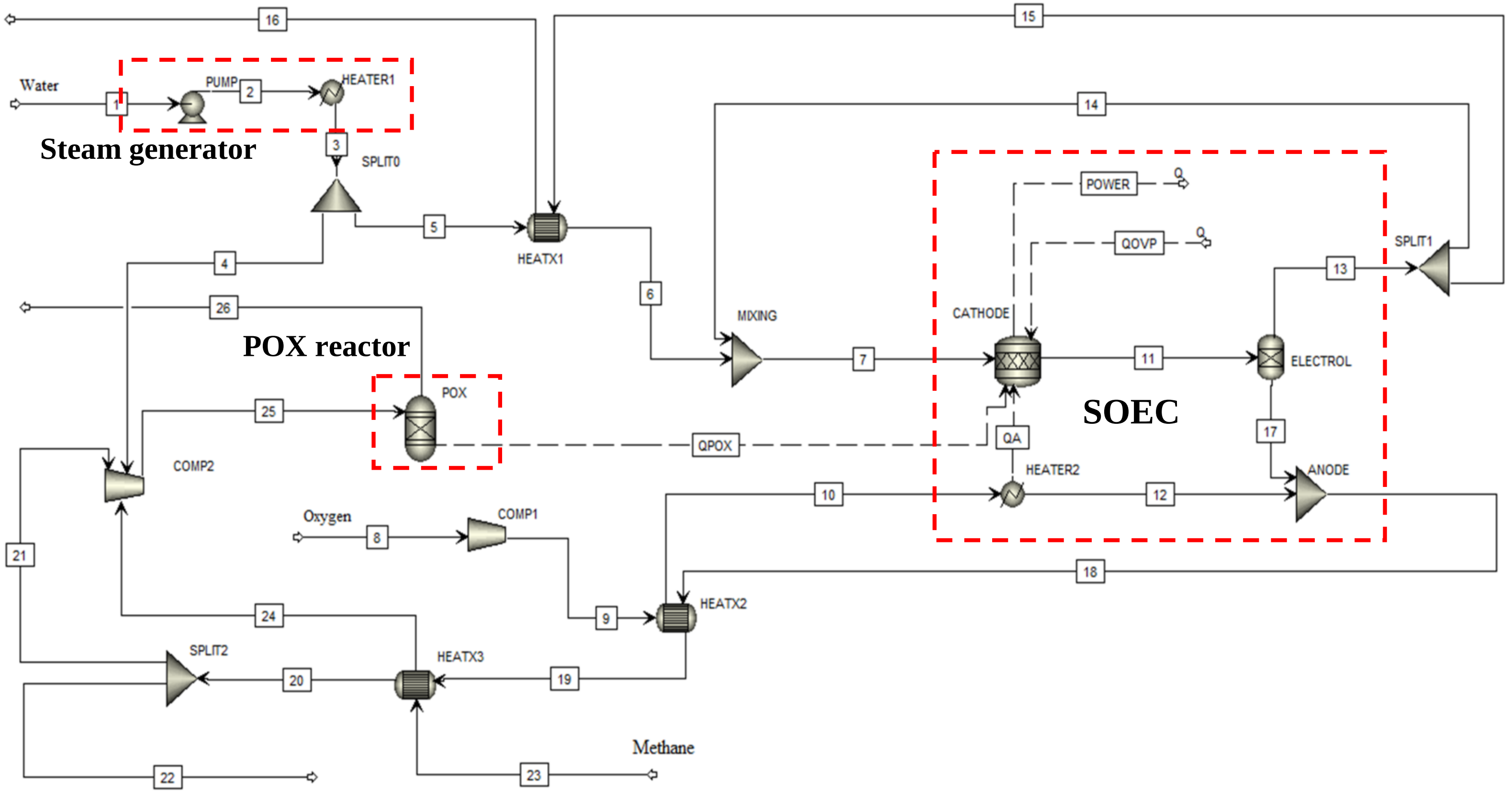

Figure 4.5 SOEC integrated with non-catalytic partial oxidation process flowsheet

CHAPTER V

SOEC PERFORMANCE AND EFFICIENCY EVALUATION

This chapter presents effect of operating parameter of SOEC on SOEC performance and efficiency. The analyzed parameters in this work are SOEC operating temperature, operating current density, steam concentration, sweep gas type and number of cells. In terms of SOEC performance, it is analyzed with equilibrium voltage, overpotential, cell voltage, heat of overpotential, utilization factor, electrical power and external heat. The results of this chapter are discussed as below.

5.1 Effect of SOEC operating temperature on SOEC performance

As temperature is the most important factor for increment of SOEC performance, effect of temperature on the performance is studied in this work. The temperature for studying is set in range of 1073 to 1273 K because it is SOEC operating temperature range. Moreover, steam to hydrogen ratio is specified as 90 to 10, current density of 2500 A/m^2, number of cells of 500 cells and oxygen as sweep gas at anode. The SOEC flowsheet process is shown in Figure 4.3. For the simulation result, it shows that increasing of temperature led to reduction of equilibrium voltage and overpotentials showed in Figure 5.1. For the reason of equilibrium voltage, according to thermodynamic of electrochemical reaction of steam, increasing of temperature can increase thermal energy but reduce electrical energy for the reaction. For the reason of each overpotential, activation overpotential decease with increasing temperature because increasing temperature effect to increase chemical kinetic energy of steam electrochemical reaction which result to increase chemical reaction rate. For the ohmic overpotential, it is reduced by increasing temperature because resistance of ionic conductivity in electrolyte layer decreases while temperature increases. This overpotential is the most important factor that effect to SOEC performance because it is the highest overpotential. Finally, the concentration overpotential is a factor that has opposite result with other overpotential because this overpotential increases with increasing temperature. This is because increasing of temperature results in increasing of effective diffusion coefficient of steam which can increase molar diffusion rate. This leads to high resistance of mass transfer between electrode and electrolyte.

Figure 5.1 showed that the activation and ohmic overpotentials are more important than concentration overpotential. Therefore, overall overpotential is decreased by increasing temperature which can also reduce cell voltage of SOEC. Thereby, electrical power used for the reaction is reduced with increasing cell temperature or thermal energy which is performed in Figure. 5.2. However, increment of cell temperature increases total energy demand, overall energy for the reaction, slightly. This is because when cell temperature is increased, the system must use more energy to take place the reaction. Hence, it can be concluded that SOEC efficiency reduces slightly when cell temperature is increased, shown in Figure 5.3. In addition, increasing temperature can decrease heat of overpotential because heat of overpotential depends on overpotential. However, increasing temperature does not affect utilization factor because increasing thermal energy can compensate electrical energy for taking place the reaction, performed by Figure 5.3.

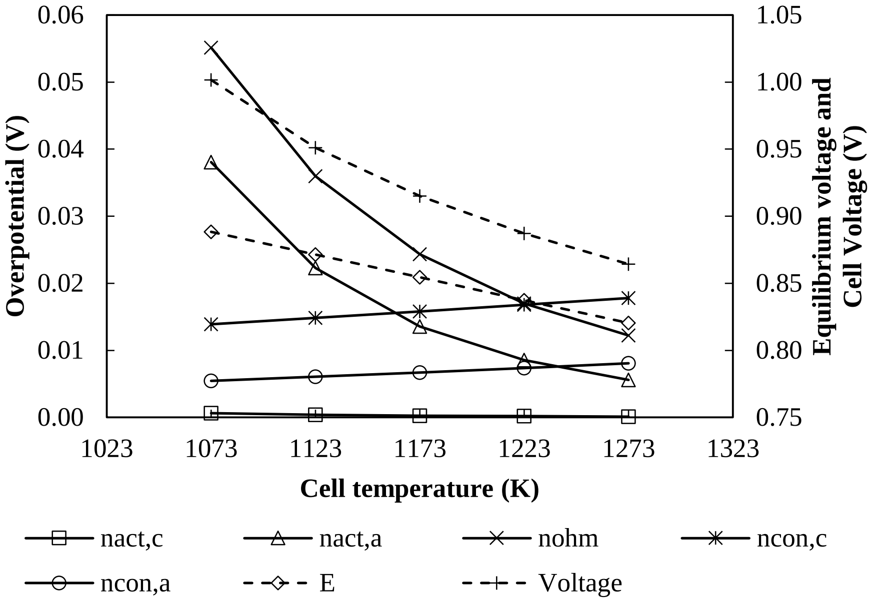

Figure 5.1 Effect of temperature on equilibrium voltage and overpotentials

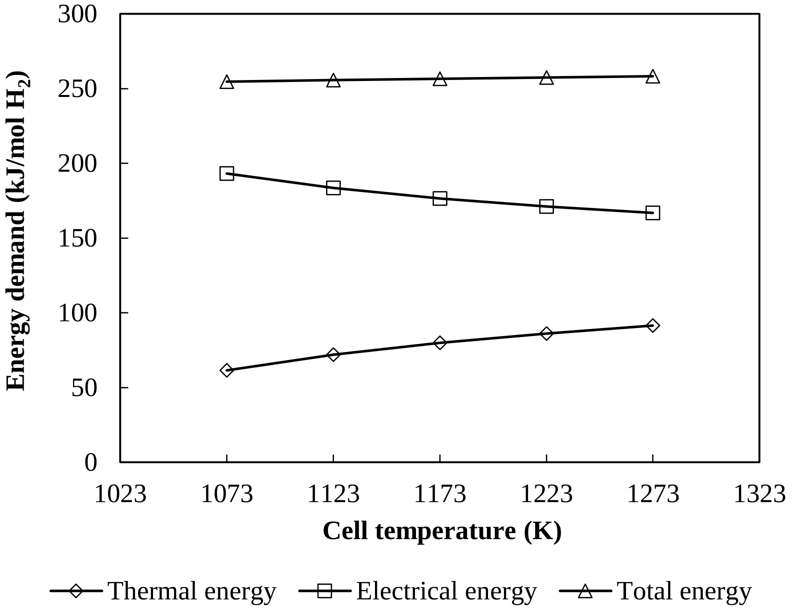

Figure 5.2 Effect of cell temperature on energy demand for the reaction

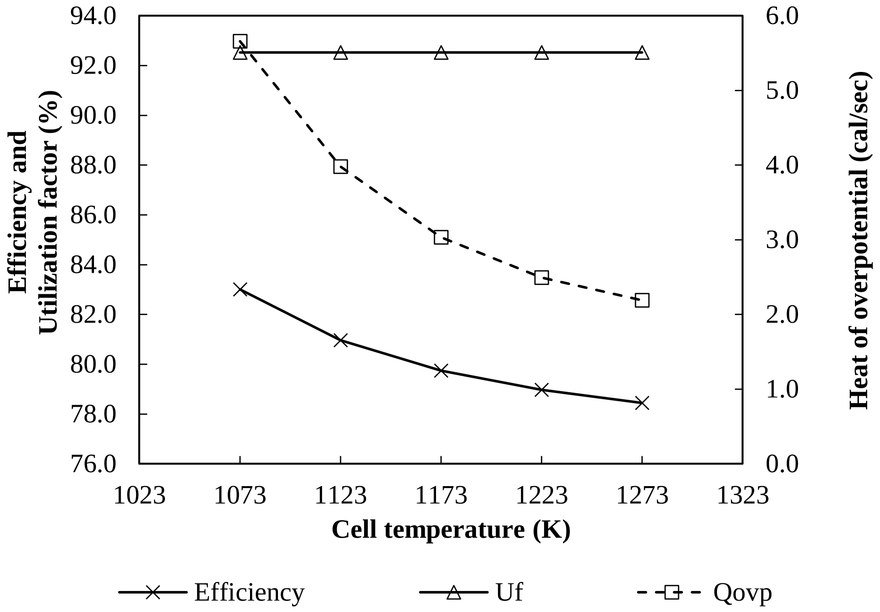

Figure 5.3 Effect of temperature on efficiency utilization factor and heat of overpotential

5.2 Effect of current density on SOEC performance

In addition to temperature, current density is also parameter that affects performance of SOEC. For the condition of simulation, cell temperature of SOEC at 1273 K, steam concentration at 90 %, oxygen as sweep gas and number of cells of 500 cells. The current density is used in range of 500 to 2500 A/m^2 because current density of SOEC in the practice is operated in low range of current density.

However, current density affect in opposite way with temperature because overpotentails is increased by increasing of current density showed in Figure 5.4. Each overpotentials type depends on current density, so increment of current density effects to increasing of overpotential. Especially, cathode concentration overpotential is the highest overpotential because SOEC is operated at temperature of 1273 K which affects cathode concentration overpotential as main overpotential. Nonetheless, Figure 5.4 noted that equilibrium voltage does not depend on current density. This is because Nernst equation, which is an equation for equilibrium voltage calculation, is used to predict minimum electrical voltage for the reaction at any resistance or concentration of reactant. Therefore, it can be concluded that increasing of current density effect to increase cell voltage, performed in Figure 5.4, which result to increase electrical power of SOEC, showed in Figure 5.5.

According to mention, the overall overpotential is increased with increasing of current density. This leads to increasing of heat of overpotential, which is shown in Figure 5.5. Moreover, increased current density can increase utilization factor which can increase hydrogen production rate. This can result to increasing of SOEC efficiency, shown in Figure 5.5. Hence, when electrical power and utilization factor of the reaction is increased with increasing of current density, thermal energy can be increased. Therefore, in terms of selecting of current density, it should be operated following by operating cost of electrical energy as well as number of cells for specified hydrogen production.

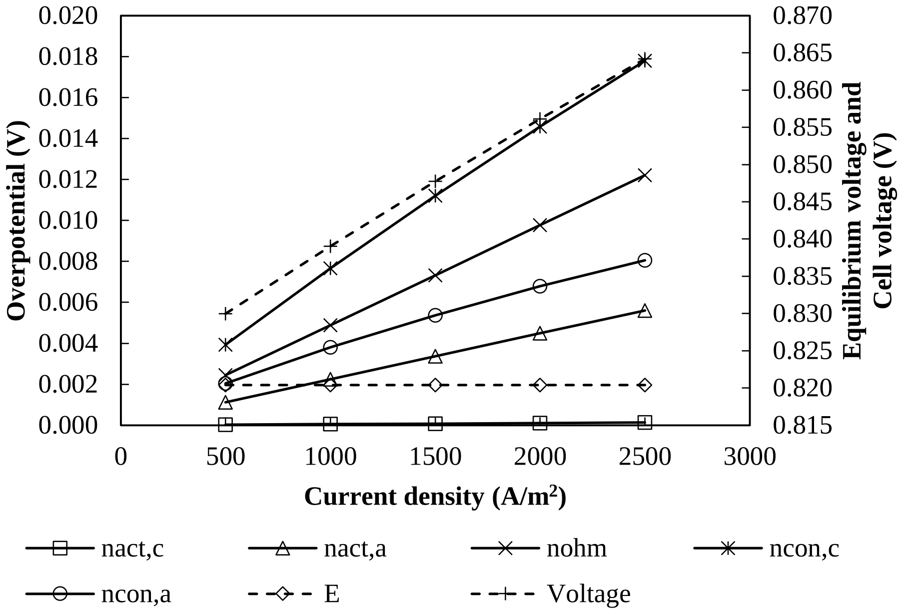

Figure 5.4 Effect of current density on equilibrium voltage and overpotentials

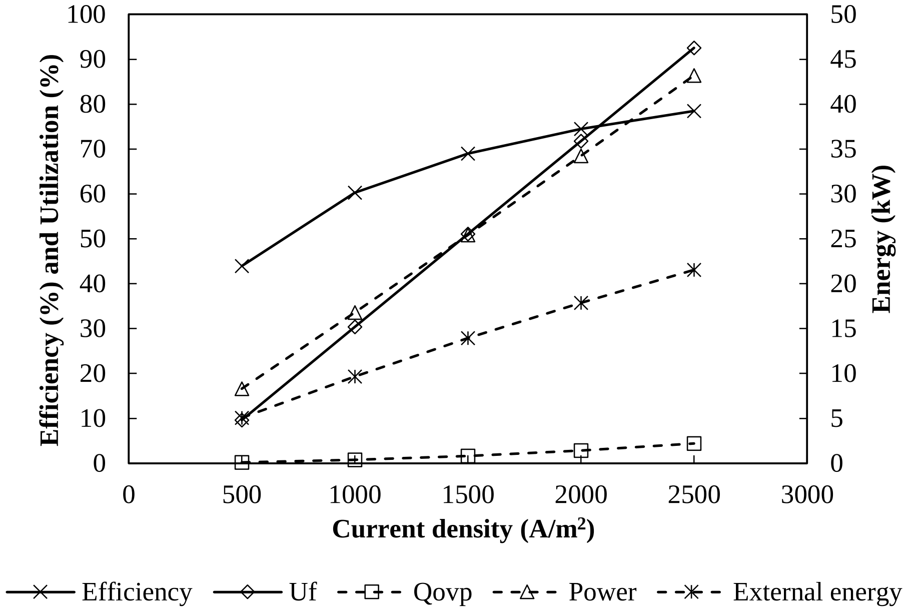

Figure 5.5 Effect of current density on efficiency, utilization factor, heat of overpotential, electrical power and external energy of SOEC

5.3 Effect of steam concentration on SOEC performance

Steam concentration can be increased by adjusting steam to hydrogen ratio which is varied in range of 50 to 90, temperature at 1273 K, current density at 2500 A/m^2, number of cells of 500 cells and oxygen as sweep gas.

For the simulation results, increment of steam concentration can bring about equilibrium voltage, which is shown in Figure 5.6, because decreasing steam concentration is a reduction of partial pressure of steam but partial pressure of hydrogen is increased. Hence, equilibrium voltage must be increase, when steam concentration is increased. For the overpotentials, Figure 5.6 is showed that cathode concentration overpotential is only overpotentials affected by increasing steam concentration. This is caused by increasing of molar diffusion rate in cathode channel. However, increment of cathode concentration is small when compare with decreasing of equilibrium voltage. Therefore, increasing steam concentration can reduce cell voltage and electrical power, which are presented by Figure 5.7. In the opposite way, when electrical energy is reduced, external energy is increased in order to balance energy in SOEC. Nonetheless, although cell voltage reduces, overpotential is increased by increasing steam concentration which leads to increasing of heat of overpotential, shown in Figure 5.7. In this work, steam concentration is adjusted by recycling of product which contains hydrogen and some steam that does not take place the reaction. For this reason, when steam concentration is increased, amount of steam is low. Hence, utilization is increased when steam concentration increases, shown in Figure 5.7. However, although utilization factor increases, produced hydrogen is quite constant. This is because amount of steam is reduced; on the other hand, utilization is increased at high steam concentration. Therefore, it can summarize that high steam concentration has high efficiency, performed in Figure 5.7, because electrical energy is reduced at high steam concentration. For these reasons, they can support that high steam concentration is the best choice for decreasing electrical energy which can effect to reduce operating cost.

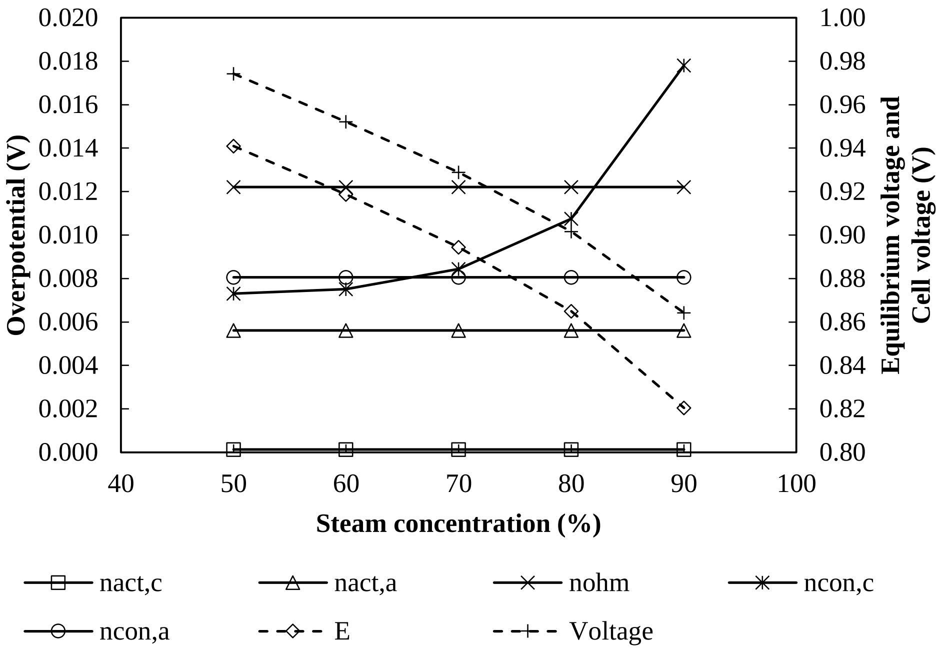

Figure 5.6 Effect of steam concentration on equilibrium voltage, overpotentials and cell voltage

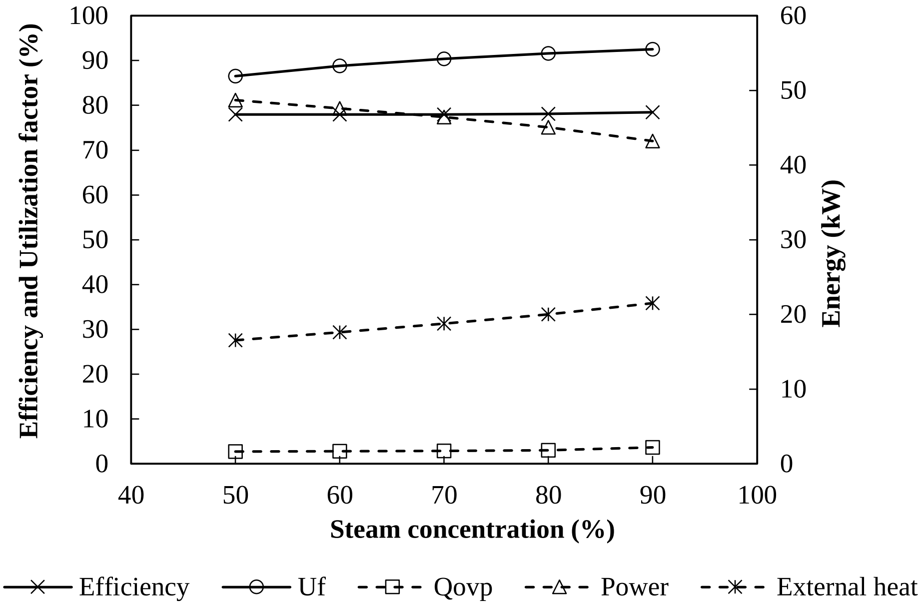

Figure 5.7 Effect of steam concentration on voltage, efficiency, heat of overpotential, hydrogen production, electrical power and external energy of SOEC

5.4 Effect of sweep gas type on SOEC performance

Sweep gas is used to displace or sweep accumulated oxygen at anode channel. In this work, sweep gases are studied by varying 3 types of sweep gas which are oxygen, air, and steam because these sweep gas can be used easily and general substance. For the condition of simulation, cell temperature of SOEC at 1273 K, current density at 2500 A/m^2, and steam concentration at 90 %.

For the result of simulation, among of these sweep gas, oxygen is a sweep gas that has the highest equilibrium voltage, secondary's is an air and the lowest equilibrium voltage is steam which are shown in Figure 5.8. As equilibrium voltage depends on partial pressure of oxygen, high oxygen content in SOEC effect to high equilibrium voltage. For the used oxygen as sweep gas, it affects only anode channel due to where oxygen flow, so it affects partial pressure of oxygen as 1 which affect the highest equilibrium voltage. For the air, it can reduce partial pressure of oxygen because the air contains 21 % oxygen and 79 % nitrogen. However, steam is the best sweep gas that can reduce partial pressure of oxygen in SOEC for the lowest equilibrium voltage since steam has not partial pressure of oxygen. On the other hand, in terms of overpotential, oxygen has the lowest overpotential, air has higher and steam has the highest overpotential which these are shown in Figure 5.8. Nevertheless, increased overpotential is only anode concentration overpotential because partial pressure of oxygen at anode channel is changed. As used oxygen as sweep gas can increase partial pressure of oxygen as 1 at anode channel, so anode concentration overpotential can be reduced. For the air and steam, these sweep gases can decrease partial pressure of oxygen in anode channel. For this reason, the anode concentration overpotential is increased by using air and steam as sweep gases. Due to the fact that air contains oxygen and nitrogen molecules but steam does not contain oxygen molecule, so steam is a sweep gas that has higher overall overpotential than air. According to discussion, although oxygen is a sweep gas that has the lowest overpotentials, steam is a sweep gas that has the lowest equilibrium voltage. Therefore, steam is the best sweep gas that can reduce electrical energy of SOEC which is shown in Figure 5.8. However, sweep gas does not affect utilization factor, shown in Figure 5.9, because sweep gas does not occur the reaction.

As discussed, it can be concluded steam is high overpotential which leads to increasing of heat of overpotential. Hence, this can reduce external heat that use for the reaction, shown in Figure 5.10. Moreover, steam require less electrical energy than other sweep gas and produced oxygen can be separated from steam easily by temperature reduction until steam is transformed to water which is liquid phase.

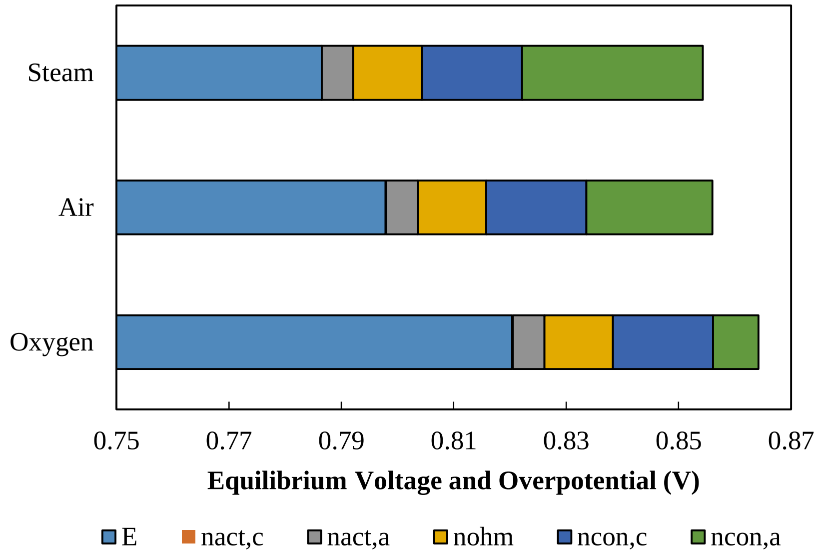

Figure 5.8 Effect of sweep gas type on equilibrium voltage and ovepotential

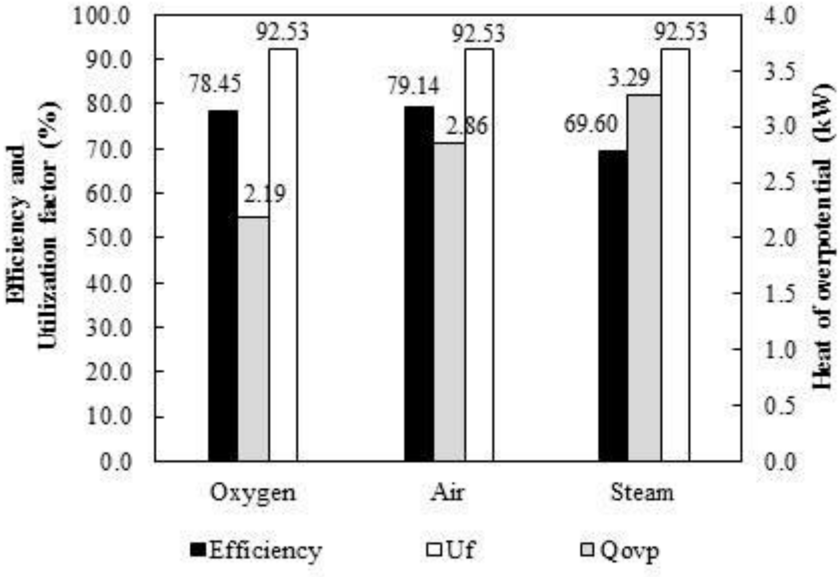

Figure 5.9 Effect of sweep gas type on efficiency, heat of overpotential, electrical power and external energy of SOEC

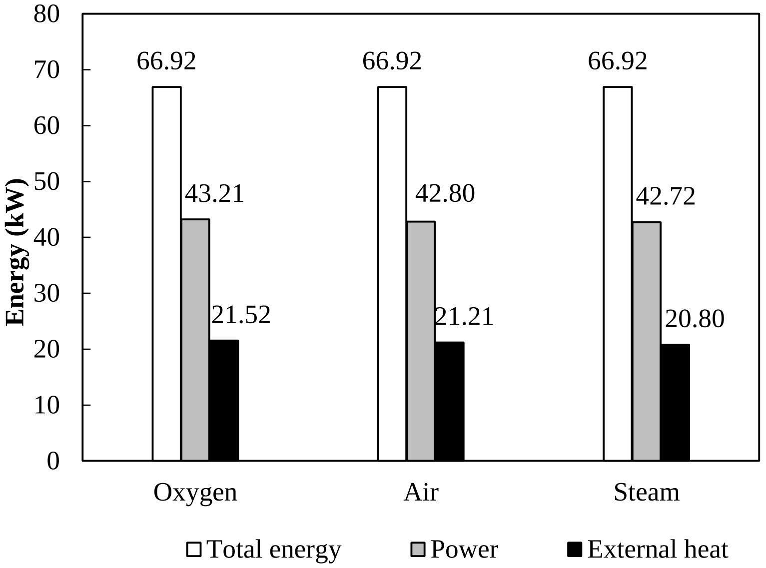

Figure 5.10 Effect of sweep gas type on efficiency, heat of overpotential, electrical power and external energy of SOEC

5.5 Effect of number of cells on SOEC performance

In this work, number of cells is varied from 100 to 500 cells in order to find that how is the effect of number of cells on SOEC performance. For the simulation result, increasing of number of cells does not affect equilibrium voltage and overpotentials because calculation of these parameters does not relate to number of cells. Although equilibrium voltage and overpotentials are not affected by number of cells, number of cells can affect electrical power resulting to increasing of electrical power with increasing number of cells, shown in Figure 5.11.

In terms of electrical power effect, the voltage can be calculated by Joule's law which is calculation based on 1 cell. In fact, SOEC must use many cells in order to increase hydrogen production rate. Therefore, increased electrical power can increase utilization factor of the reaction, performed in Figure 5.12. Consequently, external heat must increase when number of cells is increased because energy demand for the reaction is increased by increased utilization factor. Moreover, heat of overpotential is increased by increasing number of cells which is shown in Figure 5.12. For the selecting of number of cells, it must consider the operating cost that it is worth with hydrogen production rate.

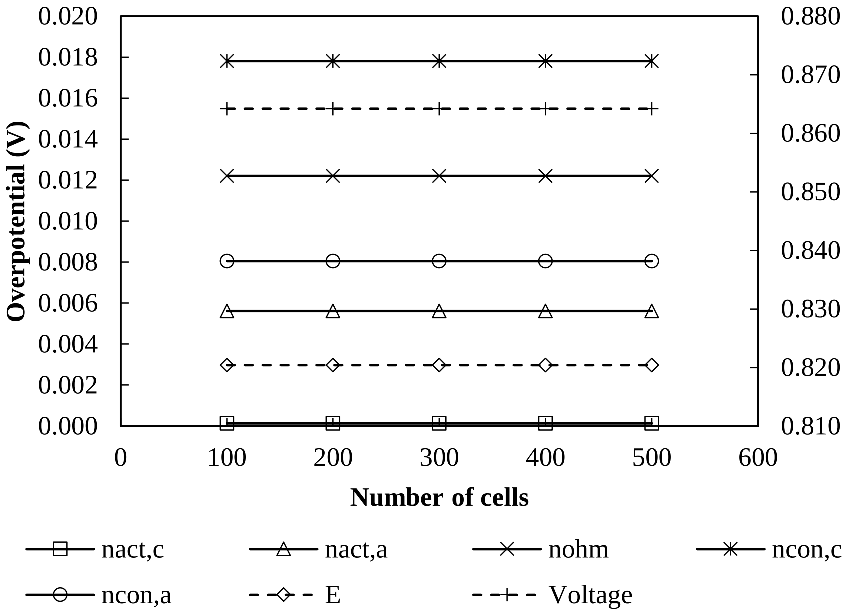

Figure 5.11 Effect of sweep gas type on equilibrium voltage and ovepotential

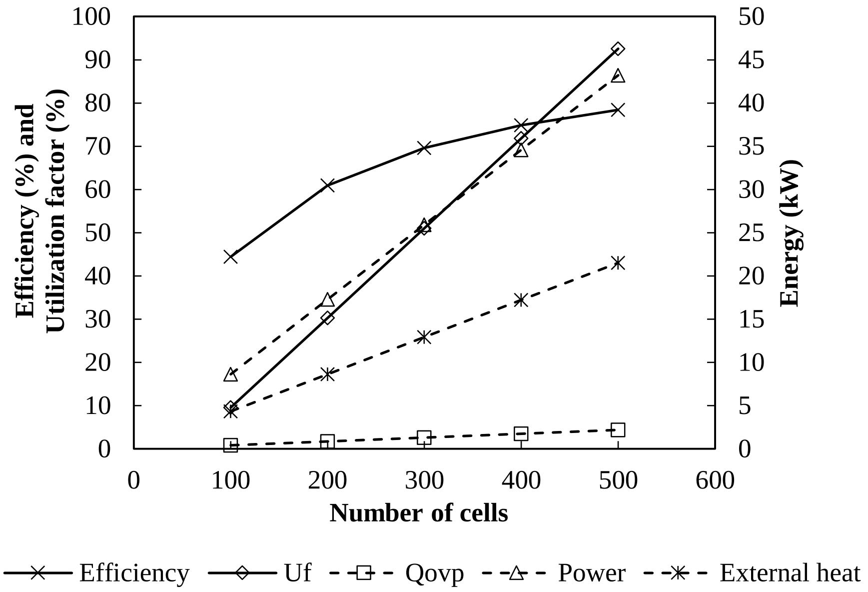

Figure 5.12 Effect of sweep gas type on efficiency, utilization factor, heat of overpotential, electrical power and external energy of SOEC

5.6 Energy consumption

SOEC uses both electrical and thermal energy for taking place electrochemical reaction. However, when these energies are calculated in term of energy consumption, it can be found that SOEC use energy higher than energy from produced hydrogen a little which is shown in Figure 5.13. Moreover, Figure 5.13 also performs that SOEC use energy for hydrogen production lower than steam methane reforming (SMR) which is commercial hydrogen production technology in this time (Jens R. et al., 2003). For this reason, SOEC is technology that has energy efficiency higher than SMR.

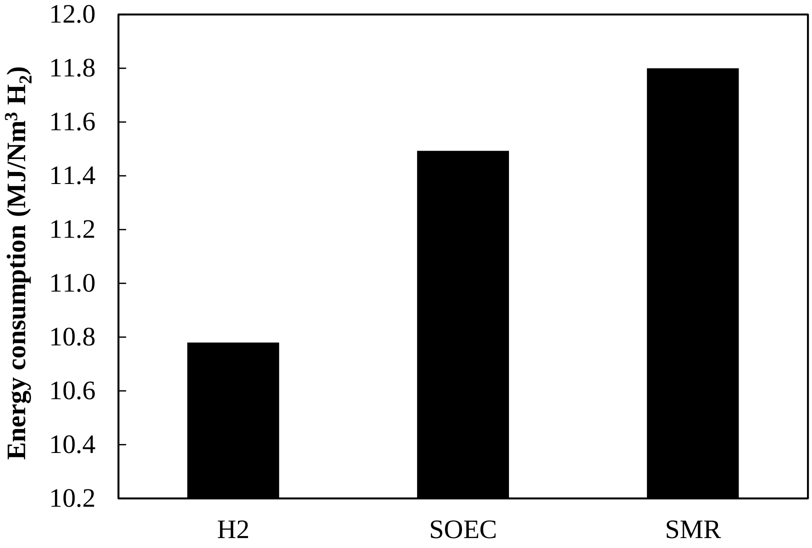

Figure 5.13 energy consumption of SOEC and SMR and energy of hydrogen

5.7 Conclusion

According to discussion, it can conclude that the voltage and overall overpotential decreased with increasing cell temperature because of low ohmic and activation overpotentials. Furthermore, it can be also observed that the ohmic and activation overpotentials provide the large contribution to overall overpotential while concentration overpotentials can be negligible when low temperature operation. However, high temperature operation must use high total energy than low temperature which result in decreasing efficiency when operate at high temperature. However, Increasing temperature does not affect utilization factor of electrochemical reaction. In terms of current density, increasing of current density led to increment of electrical power and overall overpotential. This can effect to increasing of heat of overpotential. Moreover, it can also increase utilization factor which results in high efficiency and external heat for the reaction. However, a selecting of current density, it should be operated following by operating cost of electrical energy as well as number of cells for specified hydrogen production. For the steam concentration, when steam concentration is increased, equilibrium voltage is decreased, while the overpotential is constant, but except cathode concentration overpotential that is increased because concentration of steam is changed in cathode channel. Hence, the electrical power was decreased with increasing of steam concentration. For this reason, SOEC efficiency is increased by increasing of steam concentration. Therefore, high steam concentration is recommended for SOEC operation. In term of sweep gas type, it can be used to displace oxygen out of the anode channel. The result showed that steam is the best for electrical energy reduction because it can reduce partial pressure of oxygen in anode channel. This resulted to decreasing of equilibrium voltage. Moreover, steam can produce heat of overpotential more than other sweep gas type. It leads to decreasing of external heat which assisted to reduce operating cost.

However, SOEC must use thermal energy for operation. Therefore, the thermal energy can be provided by POX reaction because this reaction is an exothermic reaction. For this reason, next chapter will present effect of operating parameter of POX reaction on SOEC performance and efficiency.

CHAPTER VI

SOEC INTEGRATED WITH POX REACTION SYSTEM ANALYSIS

This chapter presents effect of operating parameter of POX reaction, in terms of that oxygen to carbon ratio, operating temperature and pressure, on POX and SOEC performance and efficiency. In term of POX performance, it is analyzed by using outlet molar flow rate and CO/H_2 ratio. For the SOEC performance, it is analyzed by using parameter as same as previous chapter. The result of this chapter is explained as below.

6.1 Effect of POX reaction on SOEC performance and efficiency

In the general experiment, SOEC is taken in furnace for providing thermal energy. For this reason, non-catalytic partial oxidation reaction is used as external heat source for supply thermal energy to SOEC because this reaction is an exothermic reaction which can provide heat for using in other unit. The SOEC is taken in POX reactor for operating. The process of SOEC coupling with POX reaction is shown in Figure 4.5.

The non-catalytic partial oxidation reaction in this work uses methane as fuel and oxygen. This results that oxygen to carbon ratios (O/C) is an important factor for the reaction. It is varied in range of 0.615 to 0.645 in this work. In addition to oxygen to fuel ratios, operating pressure and temperature is also important factor. In terms of operating pressure, it is varied in range of 5 to 25 bars. For the operating temperature, it is varied in range of 1373 to 1493 because this range can operate temperature of SOEC system in its range.

The operating parameter of SOEC used in this work is brought from previous chapter by using operating parameter that result in the best performance. The operating current density is 2500 A/m^2, steam concentration 90 %, number of cells is 1500 cell because of increasing inlet steam in SOEC. For the temperature, it is changed by heat of exothermic reaction from POX reaction.

6.1.1 Effect of oxygen to carbon ratio on POX and SOEC performance

For the simulation result of partial oxidation reactor, when O/C is increased, molar flow rate of each component at outlet of the reactor is changed, shown in Figure 6.1. Hydrogen and carbon monoxide are reduced because methane as reactant which is fed in the reactor is reduced. For this reason, hydrogen yield is reduced by increasing O/C ratio, presented in Figure 6.2. For the steam and carbon dioxide, both are increased slightly when O/C ratio increases because increased O/C ratio can lead to methane oxidation completely, resulting in high steam and carbon dioxide. In terms of efficiency of the reaction, it is decreased slightly by increasing of O/C ratios because of decreasing hydrogen and carbon monoxide production rate. For these reasons, they can be concluded that low O/C ratios are optimal for partial oxidation reaction of methane.

In case of SOEC performance, O/C ratios can change operating temperature of SOEC because of using heat from partial oxidation reaction as external heat for SOEC system, which is shown in Figure 6.2. For this effect, performance of SOEC can be changed by O/C ratios. In terms of overall overpotential and equilibrium voltage, they can be reduced by increasing of O/C ratios, shown in Figure 6.3. This is because increasing O/C ratios can increase SOEC operating temperature, presented in Figure 6.4. Hence, cell voltage of SOEC can be reduced as same as heat of overpotential when O/C ratios increase. As a result, system efficiency can be increased by increasing of O/C ratios, performed in Figure 6.4. Therefore, electrical energy of SOEC can be reduced, while external energy of SOEC and overall hydrogen production of system are increased.

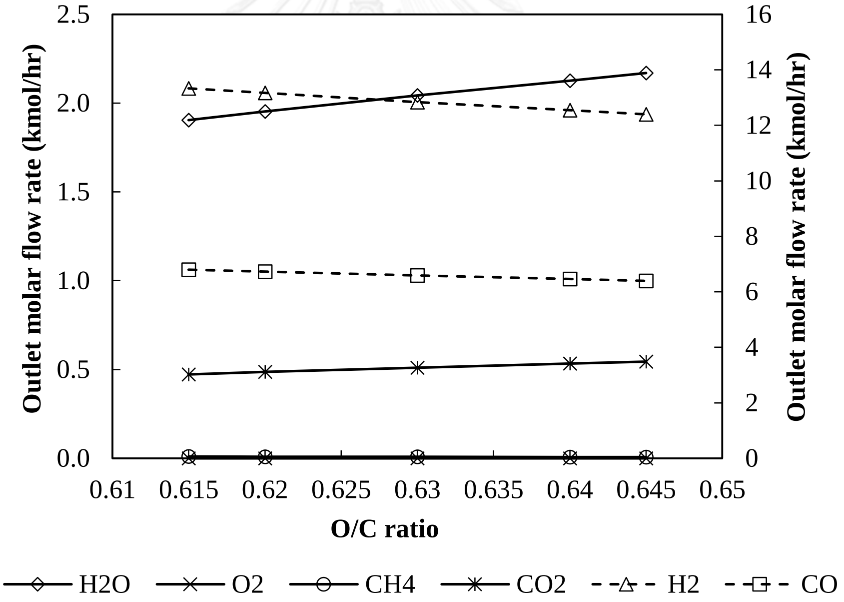

Figure 6.1 Effect of O/C ratios on outlet mole flow rate

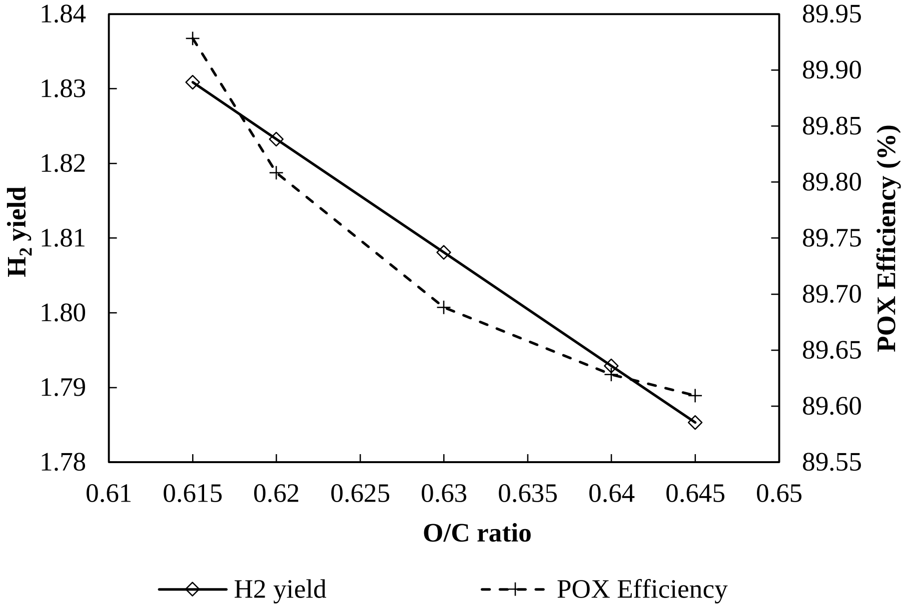

Figure 6.2 Effect of O/C ratios on H_2 yield and POX efficiency

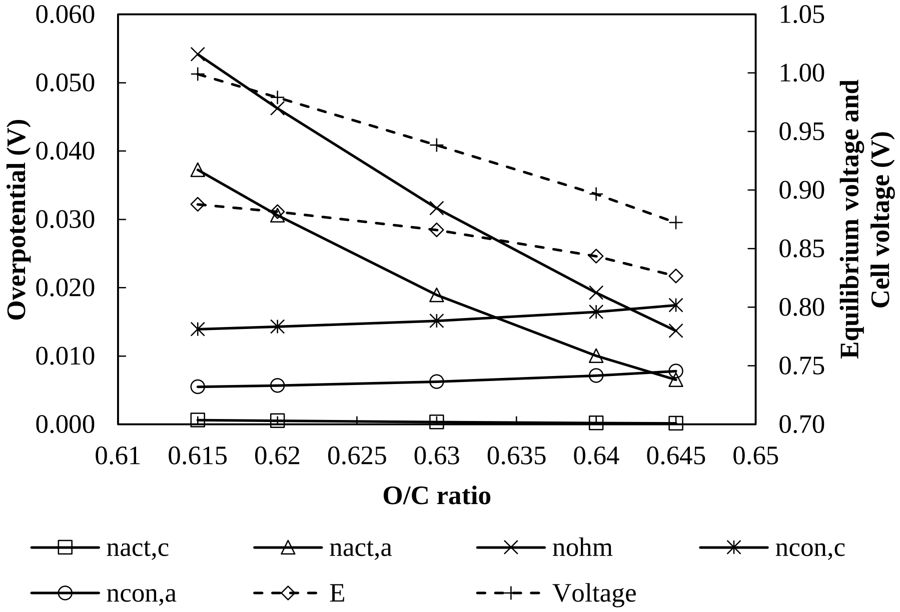

Figure 6.3 Effect of O/C ratios on equilibrium voltage, overpotential and cell voltage

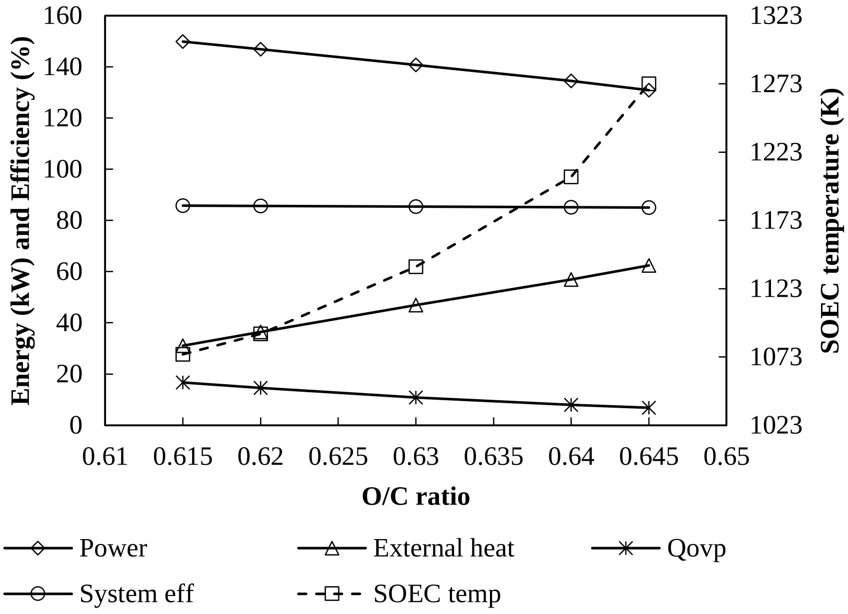

Figure 6.4 Effect of O/C ratios on power, external heat, heat of overpotential, SOEC efficiency and SOEC temperature

6.1.2 Effect of operating temperature of POX reaction on POX and SOEC performance

Effect of operating temperature of POX reaction on POX performance is shown in Figure 6.5. It finds that operating temperature affect performance of POX gradually. This is because increasing operating temperature can promote the reaction by disturbance the reaction which is exothermic reaction. When exothermic reaction is disturbed by increasing of temperature, the reaction must be reversed which result that product of the reaction is decreased. For this reason, hydrogen yield is decreased with increasing operating temperature of POX reaction, presented in Figure 6.6. Moreover, this reaction which is operated in this work has high temperature because SOEC require a high external heat for electrochemical reaction. This results in high conversion rate of the reaction for high temperature range. For this reason, it seems that efficiency of POX reaction is decreased gradually by increasing operating temperature, demonstrated in Figure 6.6.

In terms of thermal energy of POX reaction, increased POX operating temperature reduces external heat that supplies to SOEC. Due to the fact that when exothermic equilibrium reaction is disturbed by increasing temperature, the reaction favors the reverse reaction which is endothermic. For this reason, it can conclude that operation at high operating temperature reduces external energy for supplying for SOEC which results in decreasing of operating temperature of SOEC, shown in Figure 6.7. On the other hand, electrical energy of SOEC is increased when operating temperature of POX reaction increases because of operating temperature reduction of SOEC.

For characteristic of electrical energy for SOEC, according to mention that operating temperature of SOEC is reduced with increasing operating temperature of POX reaction, so both equilibrium voltage and overpotential are increased by increasing of POX reaction operating temperature which is performed in Figure 6.8. This can increase both cell voltage and heat of overpotential of SOEC. However, efficiency of system is reduced because of increasing cell voltage from increasing of operating temperature of POX reaction.

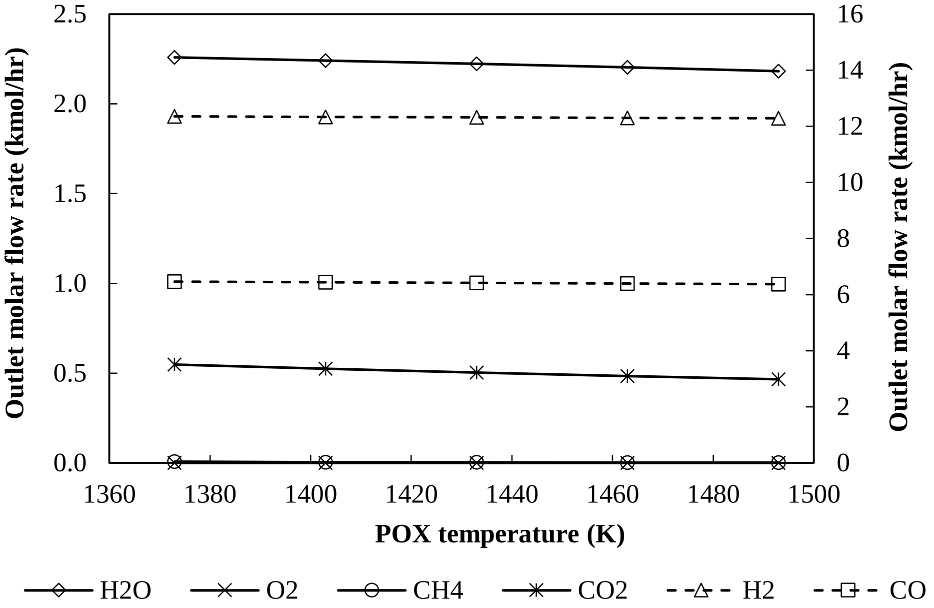

Figure 6.5 Effect of operating temperature of POX reaction on outlet mole flow rate

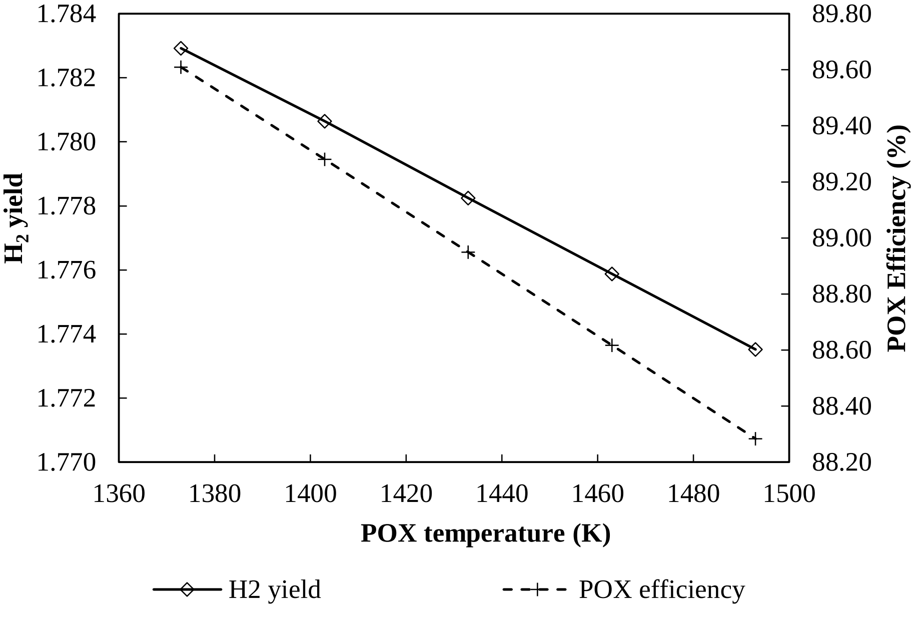

Figure 6.6 Effect of operating temperature of POX reaction on H_2 yield and POX efficiency

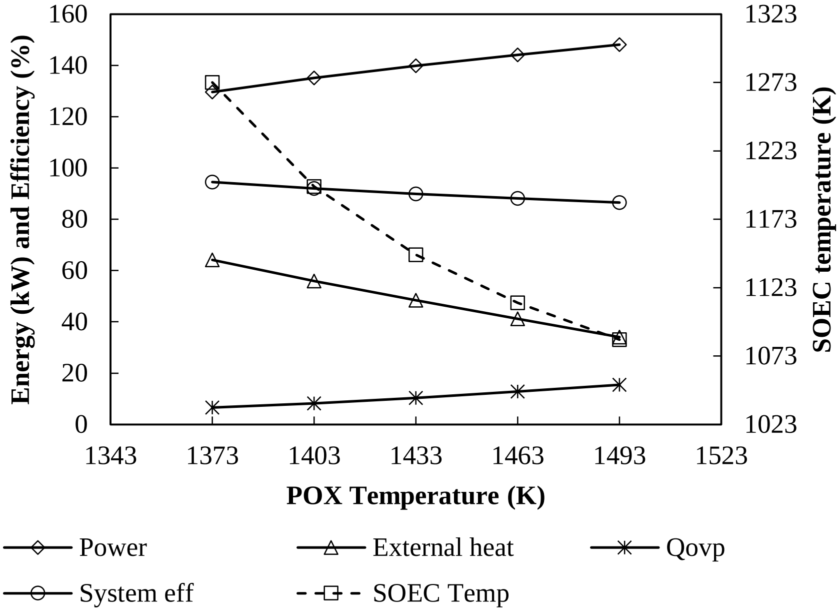

Figure 6.7 Effect of operating temperature of POX reaction on power, external heat, heat of overpotential, SOEC efficiency and SOEC temperature

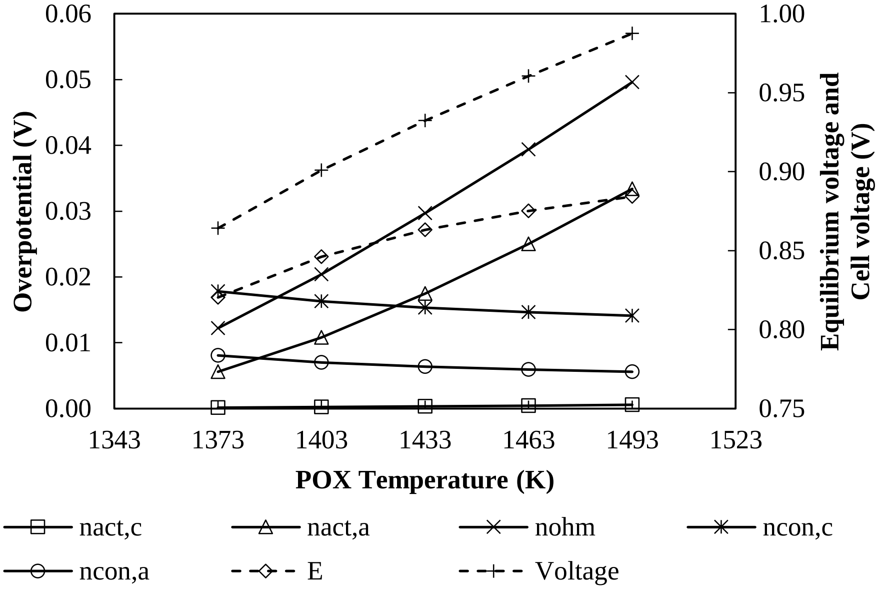

Figure 6.8 Effect of operating temperature of POX reaction on equilibrium voltage, overpotential and cell voltage

6.1.3 Effect of partial oxidation reaction operating pressure on POX and SOEC performance

For the simulation parameters, POX is operated at pressure in range of 5 to 25 atmospheric because of POX operating pressure range for the industry. The temperature of POX reaction is 1333 K at O/C ratio of 0.65. In term of effect of operating pressure of POX reaction, it can affect POX performance in term of outlet molar flow rate and POX efficiency. Because of the fact that POX reaction is an equilibrium reaction, molar flow rate of hydrogen and carbon monoxide is reduced when pressure is increased. This is because when the reaction is disturbed by increasing pressure, the reaction must be come back to equilibrium again by taking reverse reaction. This results that product of reaction is reduced while methane as reactant is increased, performed in Figure 6.9. For this reason, hydrogen yield is reduced when operating pressure of POX reaction increases which is shown in Figure 6.10. In term of POX efficiency, it is decreased with increasing of operating pressure of the reaction because produced hydrogen is reduced when operating pressure increases. For the effect of operating pressure of POX reaction on SOEC performance and efficiency, high operating pressure can release high thermal energy to surrounding which bring it to use as external energy for SOEC operation in this work because of the fact from gas’s law that temperature of gas is proportional to pressure of gas. In addition, increasing of pressure favor occur complete combustion reaction which can increase temperature of product. For these reasons, operating pressure of the reaction can affect SOEC performance. Increasing operating pressure of POX reaction can reduce equilibrium voltage and overpotential, shown in Figure 6.11, because increasing operating pressure of POX reaction can increase operating temperature of SOEC which is a main parameter for electrical energy reduction. This is result in decreasing both electrical power and heat of overpotential which are presented in Figure 6.12. However, produced hydrogen from POX reaction is reduced by increasing operating pressure. Therefore, system efficiency is reduced by increasing of operating pressure of POX reaction.

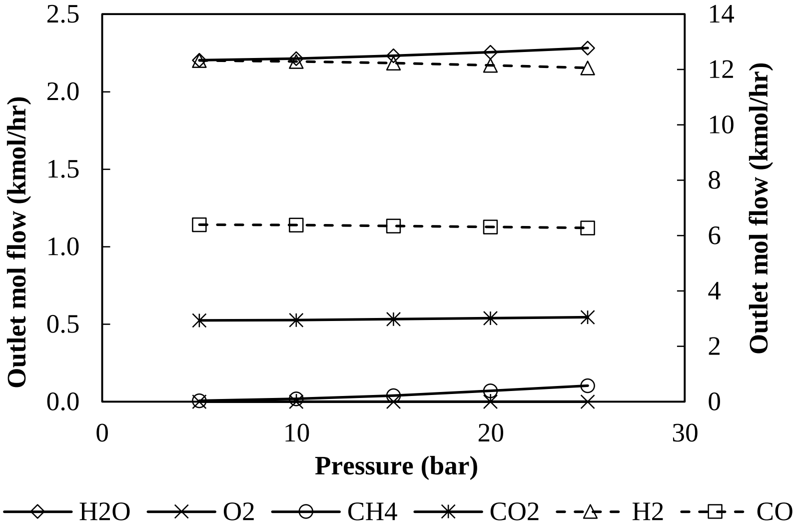

Figure 6.9 Effect of operating pressure of POX reaction on outlet mole flow rate

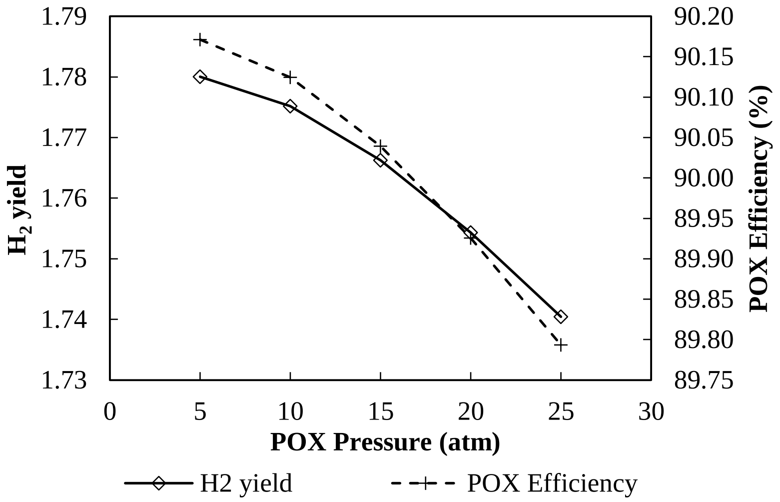

Figure 6.10 Effect of operating pressure of POX reaction on H_2 yield and POX efficiency

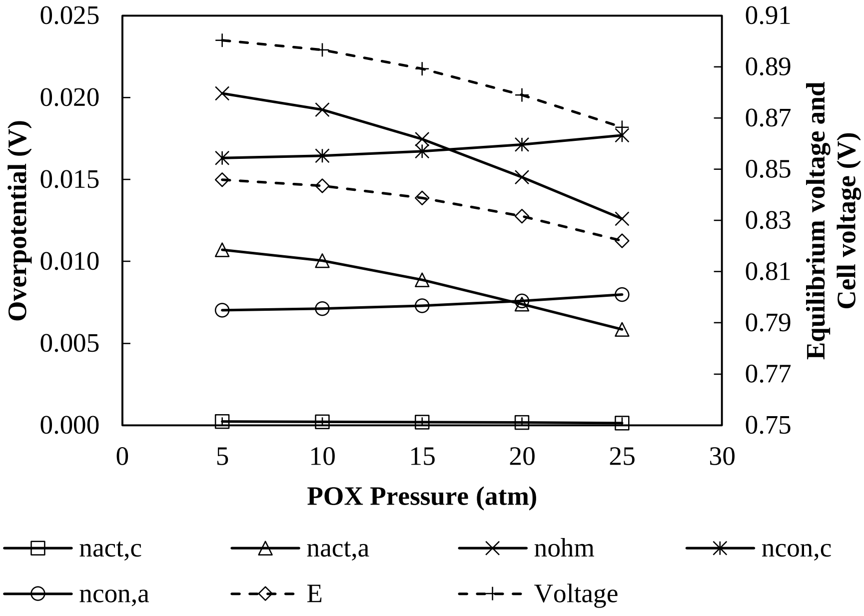

Figure 6.11 Effect of operating pressure of POX reaction on equilibrium voltage, overpotential and cell voltage

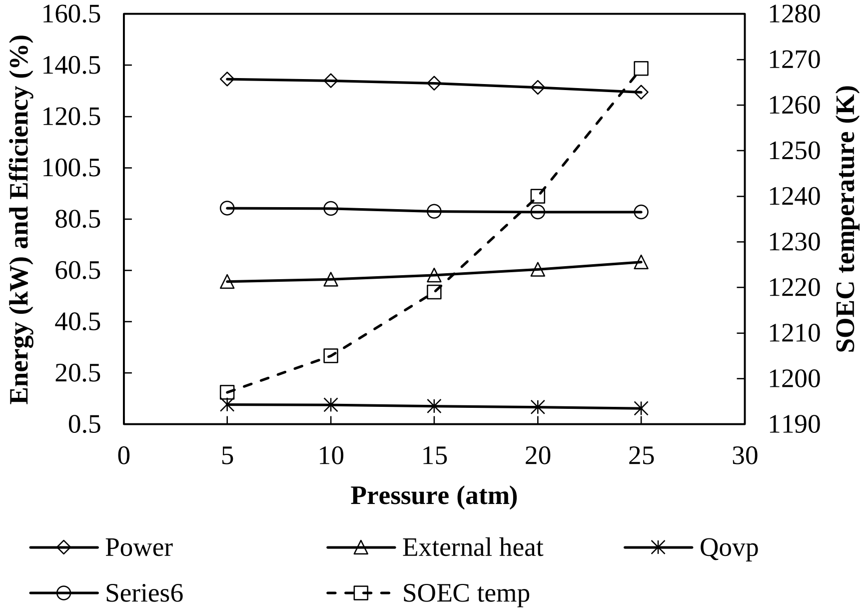

Figure 6.12 Effect of operating pressure of POX reaction on power, external heat, heat of overpotential, SOEC efficiency and SOEC temperature

6.2 Comparison of efficiency of SOEC system, and SOEC integrated with POX reaction system (SOEC-POX)

As discussed, SOEC system use both electrical and thermal energy for hydrogen production which this system can produce a little hydrogen when compare with POX reaction. This results that SOEC system has energy efficiency lower than POX reactor. Therefore, when SOEC is integrated with POX reactor, it can increase efficiency of SOEC, showed in Figure 6.13, because SOEC can use thermal energy from POX reaction which is exothermic operation. Moreover, Figure 6.10 also presents produced hydrogen comparison of SOEC system and SOEC-POX. This figure shows that SOEC-POX has high efficiency and produced hydrogen than SOEC system when SOEC system is operated as same as SOEC in SOEC-POX that is number of cells of 1500 cells, operating temperature of 1273 K, operating current density of 2500 A/m^2, steam concentration of 90 % and oxygen as sweep gas. For the POX operation, because SOEC cannot operation at high pressure, so POX should be operated at low pressure that is 5 bars, operating temperature of 1373 and O/C ratio of 0.645. These operating parameters can enhance the SOEC performance which results in low electrical energy for the reaction. Even though SOEC-POX system has higher efficiency and produced hydrogen than SOEC system, SOEC-POX system has also higher carbon dioxide emission. For this reason, this process should be evaluated carbon dioxide emission which is discussed in next topic.

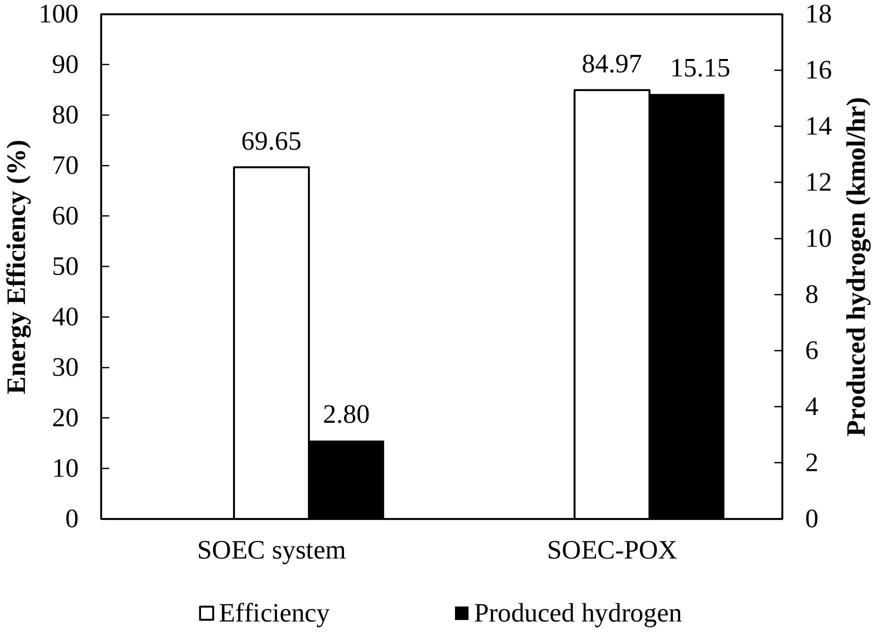

Figure 6.13 Efficiency and hydrogen product comparison of SOEC system, POX reactor and SOEC-POX

6.3 CO_2 emission comparison between SOEC integrated with POX reaction system and conventional hydrogen production system.

When SOEC is integrated with POX reaction for performance improvement, it leads to carbon dioxide and carbon monoxide production. This results that this system is not clean system. For this reason, this system should be evaluated CO_2 emission in order to confirm that this system can produce hydrogen that emits lower CO_2 than conventional hydrogen production process. The conventional hydrogen production process that is used in this work is steam reforming of methane process. The result of carbon dioxide emission comparison is presented in Figure 6.14 by using condition that is explained previous paragraph. The result shows that CO_2 emission before water gas shift reaction (WGS) is low amount, while CO emission is high quantity. However, when CO in the system is converted to CO_2 and H_2 by WGS reaction which is operated at the highest CO conversion, it results to high CO_2 emission. For this reason, this system can produce hydrogen that has lower CO_2 emission than conventional hydrogen production system. Nonetheless, this study specifies low number of cells and operating current density which result in low utilization factor of SOEC of 0.5. Therefore, this system should increase utilization factor in order to decrease CO_2 emission. The result of increased utilization factor shows in Figure 6.15. This result presents that CO_2/H_2 ratio of the system is reduced when utilization factor of SOEC is increased to 0.8.

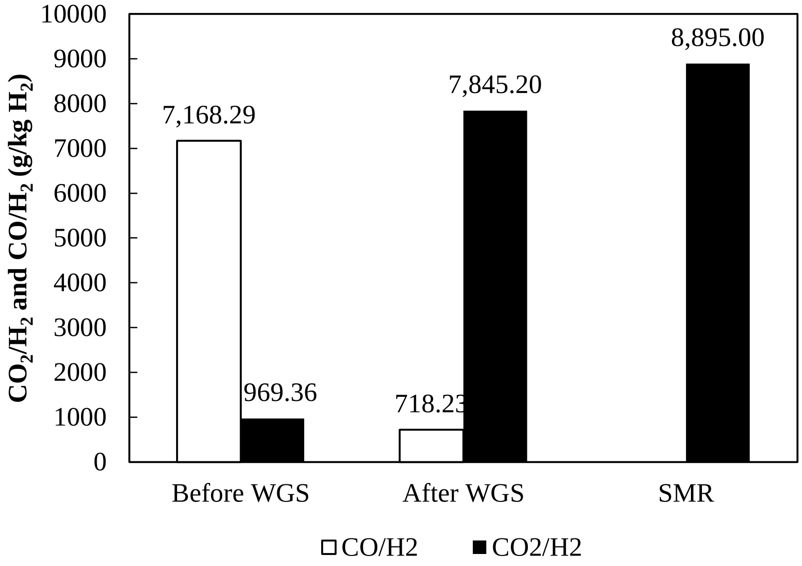

Figure 6.14 CO_2/H_2 and CO/H_2 ratio comparisons of SOEC-POX at SOEC utilization factor of 0.5 with conventional steam methane reforming plant.

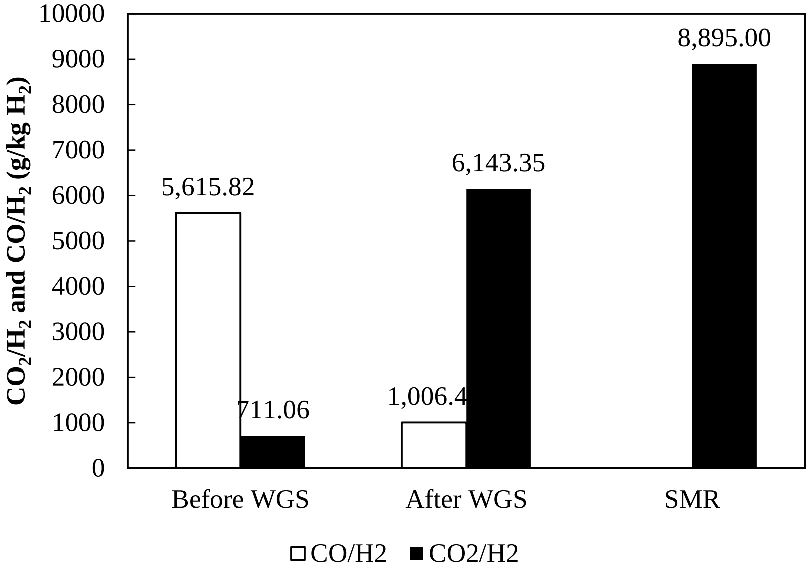

Figure 6.15 CO_2/H_2 and CO/H_2 ratio comparisons of SOEC-POX at SOEC utilization factor of 0.8 with conventional steam methane reforming plant.

6.4 Conclusion

According to discussion, SOEC integrated with POX reactor can increase efficiency of system because SOEC require thermal energy for electrochemical reaction which this thermal energy can be provided by POX reaction which is exothermic reaction. For this reason, it should be investigated effect of operating parameters of POX reaction, which are O/C ratio, operating temperature and pressure, on SOEC performance and efficiency.

For the effect of O/C ratio on POX performance, when O/C is increased, molar flow rate of each component at outlet of the reactor is changed. Hydrogen and carbon monoxide are reduced because methane as reactant which is fed in the reactor is reduced. This results to decreasing POX efficiency. In term of SOEC performance, O/C ratios can change operating temperature of SOEC because of using heat from partial oxidation reaction as external heat for SOEC system. The overall overpotential and equilibrium voltage can be reduced by increasing of O/C ratios because increasing O/C ratios can increase SOEC operating temperature. As a result, SOEC efficiency can be increased by increasing of O/C ratios.

In term of effect of operating temperature of POX reaction on POX performance, the operating temperature can affect performance of POX gradually. This is because increasing operating temperature can promote the reaction by disturbance the reaction which is exothermic reaction. When exothermic reaction is disturbed by increasing of temperature, the reaction must be reversed which result that product of the reaction is decreased. Therefore, operating temperature can affect both efficiency of POX reaction and CO/H_2 ratio by increasing slightly, For the SOEC performance and efficiency effect, operating temperature of SOEC is reduced with increasing operating temperature of POX reaction, so both equilibrium voltage and overpotential are increased by increasing of POX reaction operating temperature. For this reason, efficiency of SOEC is reduced by increasing of operating temperature of POX reaction.

For the effect of operating pressure on POX performance, molar flow rate of hydrogen and carbon monoxide is reduced when pressure is increased. This is because when the reaction is disturbed by increasing pressure, the reaction must be come back to equilibrium again by taking reverse reaction. This results that product of reaction is reduced while methane as reactant is increased which lead to increasing CO/H_2 ratio of the reaction is reduced. In addition, POX efficiency is also decreased with increasing of operating pressure of the reaction. For the effect of operating pressure on SOEC performance and efficiency, high operating pressure can release high thermal energy which leads to increasing SOEC operating temperature. Therefore, increasing operating pressure of POX reaction can reduce equilibrium voltage and overpotential. This is result in decreasing both electrical power and heat of overpotential. For this reason, SOEC efficiency can be increased by increasing of operating pressure of POX reaction.

From simulation result of SOEC-POX, it can compare efficiency and produced hydrogen with SOEC system that SOEC-POX has high both efficiency and produced hydrogen than SOEC system when SOEC system is operated as same as SOEC in SOEC-POX. This means that POX reactor can enhance SOEC efficiency and hydrogen production. However, SOEC-POX has carbon dioxide emission which result that this system is not clean system. Therefore, this system should be evaluated CO_2 emission with conventional hydrogen production process. In this work, it use steam reforming of methane as conventional hydrogen production process. From the CO_2 evaluation, it shows that this system has lower CO_2 emission than SMR. Moreover, CO_2/H_2 ratio of the system is reduced when utilization factor of SOEC increase.

CHAPTER VII

EXERGY ANALYSIS

This chapter explains exergy analysis of each unit in SOEC integrated with POX reactor. In addition, this chapter also presents effect of operating parameter of SOEC, in terms of operating temperature, operating current density, steam concentration, sweep gas type and number of cells, on SOEC exergy destruction and efficiency. The results of these studies are discussed as below.

7.1 Exergy analysis of each unit in the system

The process shown in Figure 4.5 is brought to analyze exergy of process in order to find that how is potentiality of energy using in each unit. Exergy analysis will always consider exergy destruction which is exergy loss from change of entropy in each unit when heat and work of unit is changed. The exergy analysis will be considered in each unit which the operation of each unit is explained as below.

Steam generator (SG)

Steam generator unit is used to produce steam from water by pressurizing at 5 bars and boiling at 427 K following steam table. This unit must use both electrical and thermal energy for steam production which has phase change. Therefore, this unit will always have exergy destruction.

Heat exchanger 1 (HeatX1)

Heat exchanger 1 is used to exchange heat between steam produced from steam generator and SOEC product from cathode channel to use thermal energy in the system efficiently. This unit is heat exchanging which result to change of stream entropy when changed temperature. Therefore, this unit must be analyzed exergy destruction.

Heat exchanger 2 (HeatX2)

Heat exchanger 2 is used to increase temperature of oxygen used as sweep gas by heat exchanging with SOEC product from anode channel. This is because both streams are oxygen which can exchange perfectly. Because of changed temperature as same as Heat exchanger 1, this unit must be analyzed exergy destruction.

Heat exchanger 3 (HeatX3)

Heat exchanger 3 is used to reduce temperature of oxygen from hot outlet stream from heat exchanger 2 by exchanging with methane which is used as reactant of POX reaction. Moreover, this can also increase temperature of methane which is pre-heating before it is fed to POX reactor. For this reason, Heat changer 3 require for exergy analysis.

Mixing

Mixing unit is used to mix steam with some product from cathode channel. This unit does not use both electrical and thermal energy. For this reason, this unit is not required to analyze exergy destruction.

Solid oxide electrolysis cell (SOEC)

SOEC is hydrogen production technology which is main unit of the process and this work. This unit use both electrical and thermal energy to take place steam electrochemical reaction. Therefore, this unit required to analyze exergy which will always have high exergy destruction.

POX reactor (POX)

POX reactor is used to provide thermal energy in order to supply to SOEC. In this reactor, POX reaction is taken place which is exothermic reaction. This unit will always have high exergy destruction as same as SOEC because it have high temperature and occur the reaction.

Split 0

Split 0 is used to divide steam into 2 paths which are stream for using in SOEC and POX reactor. For the splitting, it does not use both electrical and thermal energy. Therefore, the split 0 is not required for exergy analysis.

Split 1

Split 1 is equipment for splitting flow from 1 stream into 2 streams which does not change entropy of the stream. This unit is used to split some product for recycling it to adjust hydrogen to steam ratio. Moreover, this unit does not use both electrical and thermal energy. For this reason, this unit is not required to analyze exergy.

Split 2

Split 2 is equipment used to split oxygen to bring its one part to use as reactant and other is product. This unit does not uses energy for splitting substance and it does not change stream entropy, as same as split 1. Therefore, it is not required to analyze exergy.

Compressor 1 (Comp1)

Compressor 1 is used to compress oxygen to 5 bars for displacement produced oxygen. This unit use work for operation and when compress the oxygen, it will increase temperature of stream. For this reason, compressor 1 require for exergy analysis.

Compressor 2 (Comp2)

Compressor 2 is used to increase oxygen and methane pressure for preparing the operation of POX reactor. This unit use work as same as Compressor 1. Hence, Compressor 2 must be analyzed exergy destruction of the unit.

For the exergy analysis result of the process, it is an evaluation of exergy destruction of each unit operation which is shown in Figure 7.1. In addition, the efficiency of exergy is performed in Figure 7.2.

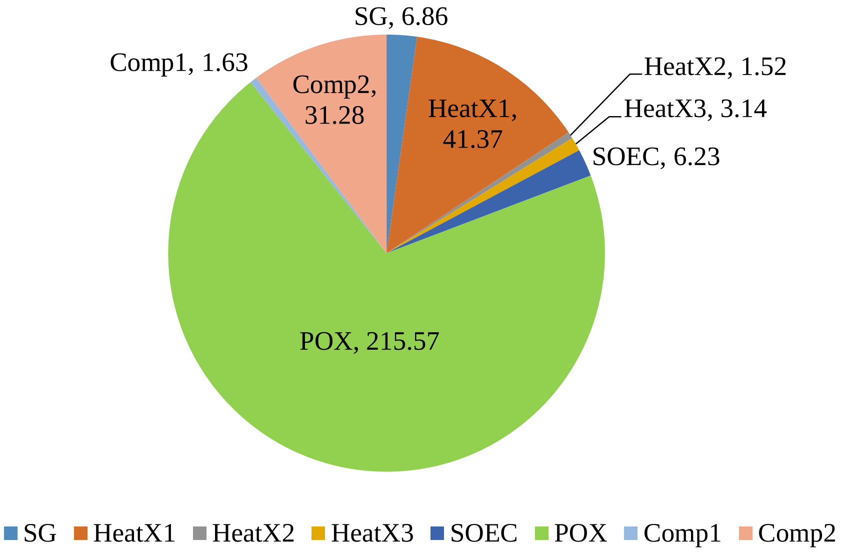

Figure 7.1 Exergy destruction of each unit in the process.

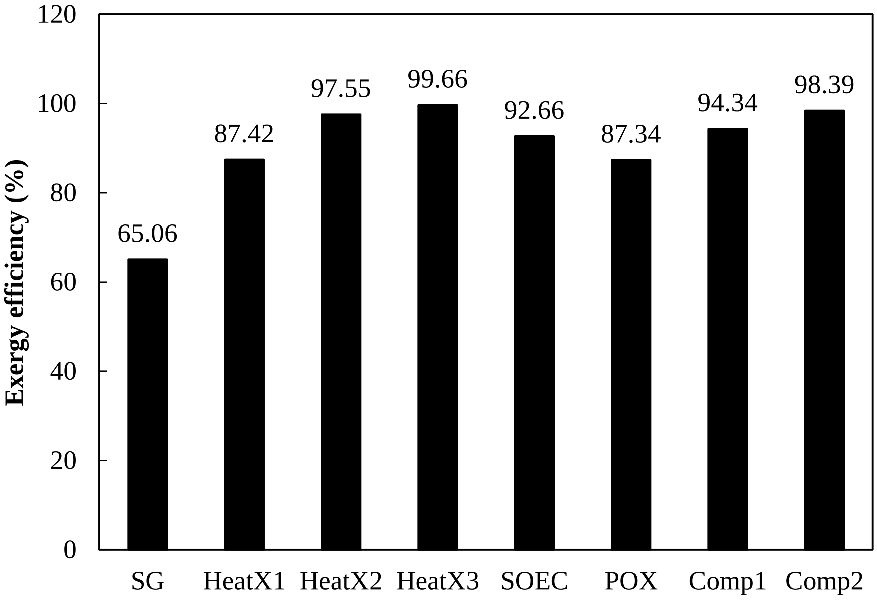

Figure 7.2 Exergy efficiency of each unit in the process.

The result showed that POX reactor is a unit that has the highest exergy destruction because this unit occurs the chemical reaction which uses methane as reactant. This reactant is a chemical substance that has the highest chemical exergy of chemical substance that use in this work. On the other hand, the produced product has low chemical exergy than methane. This results in high difference of chemical exergy between inlet and outlet which leads to low exergy efficiency.

Heat exchanger 1 is the second exergy destruction of the process. This is because this unit has high difference of temperature exchange when compared with heat exchanger 2 and 3. This affects only physical exergy which result to high physical exergy. For this reason, this unit has low energy exergy efficiency. For the heat exchanger 2 and 3 have low exergy destruction because of low different temperature exchange. However, even though heat exchanger 3 has different temperature exchange smaller than heat exchanger 2, heat exchanger 3 has exergy destruction than other. This is because heat exchanger 2 exchanges temperature by using only oxygen which result that this unit has low physical exergy. Nevertheless, heat exchanger 3 has the highest exergy efficiency because it has the lowest temperature exchange.

The third exergy destruction is compressor 2 because this unit feeds methane, oxygen and some steam into the unit. This leads to composition variation at outlet of this unit which results that chemical exergy of outlet has lower than inlet. In term of physical exergy, when gas is compressed, its volume will be small and increase its temperature. Moreover, gas will always experience friction which results that some of work that supply to the compressor will be converted into heat. This results to energy loss from compression. For these reasons, compressor 2 has high exergy destruction. For the compressor 1, it is an increase pressure of pure component that is oxygen. This affects only physical exergy which results that compressor 1 has low exergy destruction, this leads to high exergy efficiency.

Steam generator has exergy destruction because it is responsible for changing substance phase from liquid into gas phase as well as increasing of pressure which result to physical exergy. In addition, thermal energy that is used for phase changing will always loss by changing into steam. In term of chemical exergy, when water is changed into steam, the chemical exergy will always change because water and steam have different standard chemical exergy. For these reasons, this unit has low exergy efficiency.

SOEC is a unit operation that has low exergy destruction because this unit uses steam for hydrogen production which both substance has high different standard chemical exergy value. This results that exergy at outlet of SOEC will always be high. However, this unit uses both electrical and thermal energy for electrochemical reaction which use electricity as main energy. Moreover, electricity has exergy as amount of electricity that is used. This is because electricity has high potential. For this reason, energy inlet of SOEC will always high exergy. Therefore, exergy destruction of this unit is quite small. However, SOEC is sensible to operating parameter which results to exergy destruction and efficiency. Consequently, effect of operating parameter of SOEC on exergy destruction and efficicency should be investigated, which is discussed as below.

7.2 Effect of operating parameter of SOEC on exergy destruction and efficiency

SOEC is a main unit operation of this work. For this reason, SOEC is analyzed exergy in order to notice characteristic of SOEC that how are operating parameter effect on SOEC exergy destruction and efficiency. In terms of effect of temperature and operating current density, they are shown in Figure 7.3. This figure shows that when operating temperature increase, exergy destruction is increased which leads to decreasing of exergy efficiency. This is because increasing of operating temperature does not affect hydrogen production. Although increasing operating temperature can reduce electrical energy for electrochemical reaction, thermal energy for operating is increased because of energy balance of SOEC. For this reason, it can conclude that exergy destruction is increased by increasing of operating temperature which leads to reducing of exergy efficiency of SOEC. This means that energy that is used for increasing of operating temperature does not produce useful work for SOEC operation.

In term of operating current density, increasing operating current density affect exergy destruction and efficiency in opposite way of operating temperature. This is because increasing current density can increase hydrogen production rate. Although increasing current density effect to increasing of electrical energy, this energy can produce useful work which is hydrogen production. This result to low exergy destruction when operating current density is increased which leads to increasing of exergy efficiency. This is consistent with energy efficiency of SOEC.

For the result of effect of number of cells and steam concentration on exergy destruction and efficiency, they are presented in Figure 7.4. The result shows that exergy destruction is increased by decreasing number of cells and increasing steam concentration. In term of effect of number of cells, exergy destruction is increased by decreasing number of cells. This has a reason as same as current density effect which is that increasing number of cells can increase hydrogen production rate, For this reason, it can conclude that exergy destruction of SOEC is reduced with increasing number of cells which bring about increasing exergy efficiency.

Increasing steam concentration of SOEC inlet can decrease exergy destruction and increase exergy efficiency of SOEC. Due to recycling, when steam concentration is increased, amount of steam in the stream is increased. This results to decreasing utilization factor which leads to decreasing hydrogen production rate. Moreover, increasing steam concentration can reduce equilibrium voltage which can reduce electrical energy for the reaction. Therefore, increasing steam concentration can reduce exergy destruction and increase exergy efficiency.

Finally, sweep gas type, used to displace oxygen in anode channel, can affects exergy destruction and efficiency. The result of this effect is presented in Figure 7.5. It shows that steam is a sweep gas that has the lowest exergy destruction, while oxygen has the highest exergy destruction. This is because steam can reduce equilibrium voltage which results to decreasing of electrical energy for SOEC. For this reason, among of sweep gas, steam has the highest exergy efficiency.

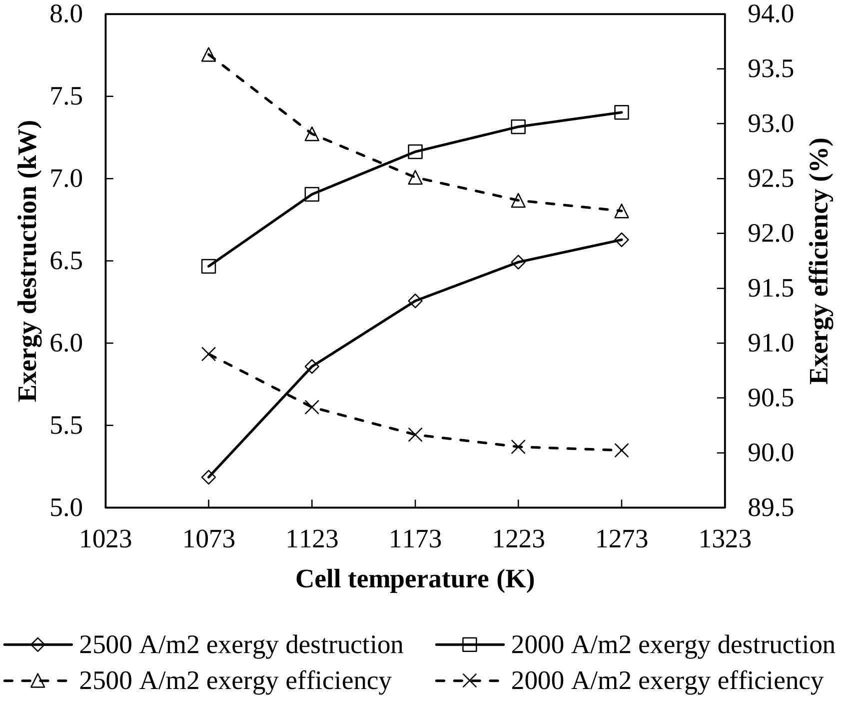

Figure 7.3 Effect of temperature and operating current density on exergy destruction and exergy efficiency

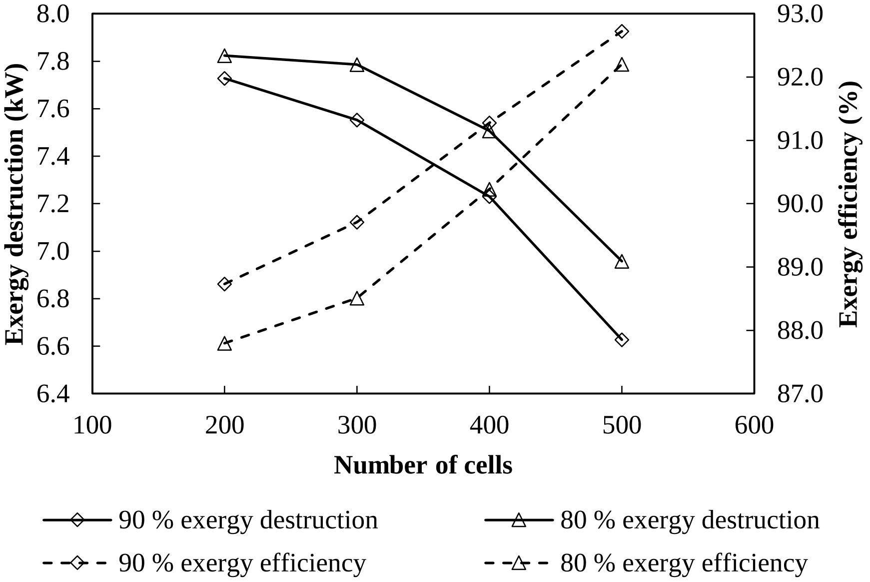

Figure 7.4 Effect of number of cells and steam concentration on exergy destruction and exergy efficiency 1 kmol/hr

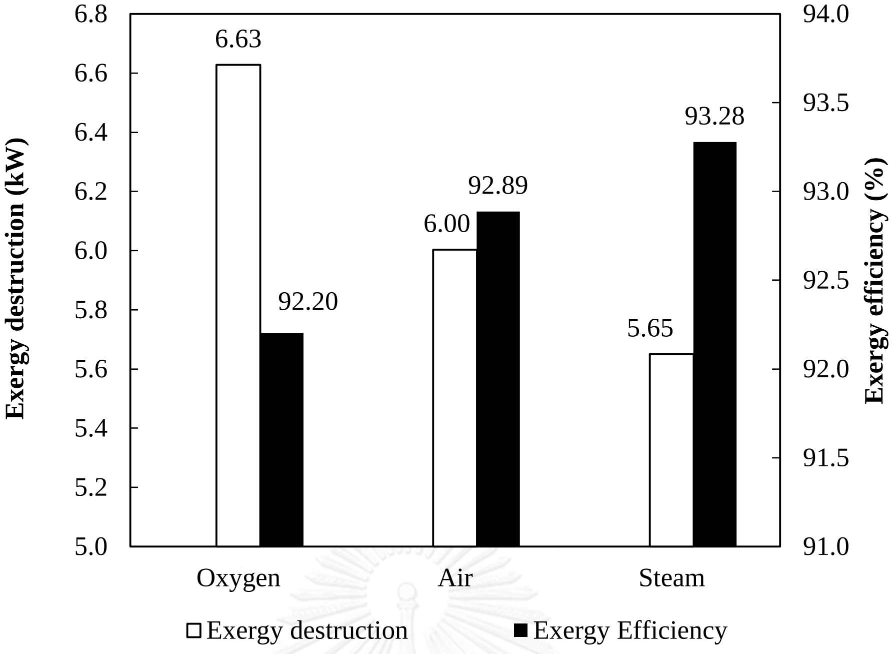

Figure 7.5 Effect of sweep gas type on exergy destruction and efficiency

7.3 Exergy destruction and efficiency comparison between SOEC and SMR

In order to know that hydrogen production by using SOEC has exergy destruction that higher or lower than conventional hydrogen production system, exergy destruction and efficiency of SOEC should be compared with SMR system which is demonstrated in Figure 7.6. The result shows that SOEC has higher exergy destruction than SMR because SOEC use electrical energy which is energy that has high exergy; on the other hand, SMR use only thermal energy which has lower exergy than electrical energy. Moreover, used electrical energy in SOEC can be transferred to thermal energy which means that it occur exergy destruction. For these reasons, SOEC has lower exergy efficiency than SMR.

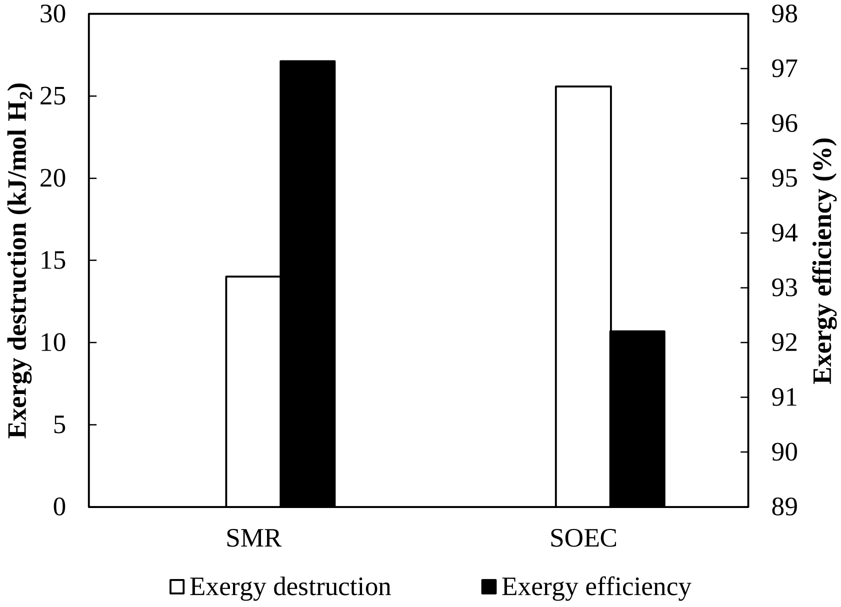

Figure 7.6 Exergy destruction and efficiency comparison between SOEC and SMR

7.4 Conclusion

This chapter is an analysis of exergy of SOEC integrated with POX reaction system. In addition, effect of operating parameter of SOEC on exergy destruction and efficiency is also investigated in this chapter. The result of these studies can be summarized as below.

Unit operation of SOEC integrated with POX reaction system that has the highest exergy destruction is POX reactor. This is because this unit occurs oxidation reaction which is a hydrogen production by using methane as reactant. For this reason, chemical exergy is a main effect from POX reactor which leads to low exergy efficiency. The second exergy destruction is a heat exchanger 1. This heat exchanger has high difference of exchanged temperature which affects only physical exergy because composition of inlet and outlet does not change. Among of heat exchanger that is used in this system, heat exchanger 2 is lowest exergy destruction because this unit uses oxygen as fluid for exchanging temperature both inlet and outlet which result to low difference of physical exergy between inlet and outlet. The third’s is compressor 2. In term of physical exergy, when gas is compressed, it experiences friction which results that some of work that supply to the compressor will be converted into heat. This results to high physical exergy. For the chemical exergy, this unit feeds methane, oxygen and some steam into the unit. This leads to composition variation at outlet of this unit which cause to high chemical exergy. While this unit has high both physical and chemical exergy, compressor 1 is affected only physical exergy since this unit uses only oxygen. For these reason, compressor 2 has higher exergy destruction than compressor 1 which leads to compressor 1 has higher exergy efficiency than compressor 2. For the steam generator unit, exergy destruction is occurred by phase changing of water into steam from increasing temperature and pressure. This affects both physical and chemical exergy. Physical exergy is changed by increasing temperature and pressure of water. Chemical exergy is changed by phase changing of water into steam because standard chemical exergy of water and steam has different value. Finally, SOEC is a hydrogen production technology. This unit uses steam as reactant and both electrical and thermal energy, which result that inlet of SOEC has high exergy. Moreover, hydrogen is chemical substance that has high standard chemical exergy. Therefore, outlet of SOEC is high exergy as same as SOEC inlet. This leads to small difference exergy between inlet and outlet which results to low exergy destruction. However, this unit is main unit of this thesis. Therefore, it should be investigated effect of operating parameter on exergy destruction and efficiency

For the effect of operating parameter of SOEC on exergy destruction and efficiency, the operating parameters for this topic are operating temperature, current density, steam concentration, number of cells and sweep gas type. In terms of the operating temperature and current density, exergy destruction can be reduced by decreasing operating temperature and current density because high operating temperature increase energy for SOEC operation which results to high exergy destruction, while increasing operating current density can increase hydrogen production rate which can reduce energy consumption to hydrogen production ratio. For the steam concentration and number of cells, increasing steam concentration and number of cells can decrease exergy destruction which leads to increasing exergy efficiency. These are because increasing steam concentration can reduce equilibrium voltage which can reduce electrical energy for operation, whereas increasing number of cells can increase hydrogen production rate as same as current density which can reduce energy consumption to hydrogen production ratio. The last effect, steam is a sweep gas that has the lowest exergy destruction which leads to the highest exergy efficiency in among of sweep gas, while oxygen has the highest exergy destruction. This is because steam has the lowest equilibrium voltage which causes to the lowest electrical energy for electrochemical reaction. For the comparison between SOEC and SMR exergy destruction and efficiency, it find that SOEC has higher exergy destruction than SMR which leads to lower exergy efficiency than SMR.

CHAPTER VIII

CONCLUSION AND RECOMMENDATION

8.1 Conclusion

The objective of this work is a SOEC simulation and investigation of effect of operating parameter of SOEC on SOEC performance and efficiency. The electrochemical model of SOEC is taken into account in SOEC simulation. The simulation result shows that characteristic of voltage and current density of SOEC between simulation and experimental data is good agreement. The effect of key operating parameters, i.e. operating temperature, operating current density, steam concentration, number of cells, and sweep gas type, on SOEC system performance and efficiency presented in this work. The result shows that increasing operating temperature can decrease electrical energy consumption. For this reason, SOEC should be integrated with exothermic reaction, which is POX reaction, in order to provide thermal energy to SOEC.

SOEC integrated with POX reaction is investigated in order to improve performance of SOEC system. The simulation must be tested effect of POX operating parameter, i.e. oxygen to carbon ratio, operating temperature and operating pressure, on SOEC performance and efficiency. The result show that SOEC integrated with POX reaction can enhance efficiency and hydrogen production. However, this system has carbon dioxide emission. For this reason, carbon dioxide evaluation is investigated in this work. As this system is operated as process, exergy analysis is evaluation in this work.

Exergy analysis is potential of energy evaluation that use in each unit. The result showed that POX reactor has the highest exergy destruction. This presents that this process should be improve performance. However, SOEC is main unit of this work. SOEC must be evaluated exergy analysis. The effect of key operating parameters of SOEC on exergy destruction and efficiency is performed in this work

8.2 Recommendation

SOEC integrated with POX reaction should be optimized in order to operate this system for low carbon dioxide to hydrogen ratio, low electrical energy and high hydrogen production.

REFERENCES

Al-Sayari, S. A. (2013). Recent Developments in the Partial Oxidation of Methane to Syngas. *Catalysis Journal, 6*, 17-28.

Albrecht, B. A., Kok, J. B. W., & Veringa, H. J. (2002). Generation of synthesis gas and power by partial oxidation of natural gas in a gas turbine.

Angeli, S. D., Monteleone, G., Giaconia, A., & Lemonidou, A. A. (2014). State-of-the-art catalysts for CH4 steam reforming at low temperature. *International Journal of Hydrogen Energy, 39*(5), 1979-1997.

Arashi, H., Naito, H., & Miura, H. (1991). Hydrogen production from high-temperature steam electrolysis using solar energy. *International Journal of Hydrogen Energy, 16*(9), 603-608.

Bhattacharya, A., Das, A., & Datta, A. (2014). Exergy based performance analysis of hydrogen production from rice straw using oxygen blown gasification. *Energy, 69*(0), 525-533.

Blake Reynolds, Riverside, & Conn. (1973). New York Patent No.: U. S. P. Office.

Dincer, I., & Rosen, M. A. (2012). *Exergy: energy, environment and sustainable development*: Newnes.

The Emissions Gap Report 2012. (2012). United Nations Environment Programme (UNEP).

Fernandes, F. A. N., Souza, C. P., & Sousa, J. F. (2006). Modeling of partial oxidation of methane in membrane reactor. *Engenharia Térmica (Thermal Engineering), 5*, 40-45.

Fujiwara, S., Kasai, S., Yamauchi, H., Yamada, K., Makino, S., Matsunaga, K., Hoashi, E. (2008). Hydrogen production by high temperature electrolysis with nuclear reactor. *Progress in Nuclear Energy, 50*(2–6), 422-426.

Ghannadzadeh, A., Thery-Hetreux, R., Baudouin, O., Baudet, P., Floquet, P., & Joulia, X. (2012). General methodology for exergy balance in ProSimPlus® process simulator. *Energy, 44*(1), 38-59.

Gundersen, T. (2009). An introduction to the concept of exergy and energy quality. *Department of Energy and Process Engineering, Norwegian University of Science and Technology, Trondheim, Norway, Version, 3*.

Guo, W., Wu, Y., Dong, L., Chen, C., & Wang, F. (2012). Simulation of non-catalytic partial oxidation and scale-up of natural gas reformer. *Fuel Processing Technology, 98,* 45-50.

Hajjaji, N., Pons, M.-N., Houas, A., & Renaudin, V. (2012). Exergy analysis: An efficient tool for understanding and improving hydrogen production via the steam methane reforming process. *Energy Policy, 42*(0), 392-399.

Harvego, E. A., McKellar, M. G., O'Brien, J. E., & Herring, J. S. (2009). Parametric evaluation of large-scale high-temperature electrolysis hydrogen production using different advanced nuclear reactor heat sources. *Nuclear Engineering and Design, 239*(9), 1571-1580.

Hawkes, G. L., O'Brien, J. E., Stoots, C. M., Herring, J. S., & Shahnam, M. (2005). *CFD model of a planar solid oxide electrolysis cell for hydrogen production from nuclear energy*.

Huang, J., & Dincer, I. (2014). Parametric analysis and assessment of a coal gasification plant for hydrogen production. *International Journal of Hydrogen Energy, 39*(7), 3294-3303.

Hydrogenics. (2014). HySTAT® HYDROGEN GENERATORS.

Iaquaniello, G., Antonetti, E., Cucchiella, B., Palo, E., Salladini, A., Guarinoni, A., Ba, L. (2012). Natural Gas Catalytic Partial Oxidation: A Way to Syngas and Bulk Chemicals Production.

Khoshnoodi, M., & Lim, Y. S. (1997). Simulation of partial oxidation of natural gas to synthesis gas using ASPEN PLUS. *Fuel Processing Technology, 50*(2–3), 275-289.

Li, Q., Zheng, Y., Guan, W., Jin, L., Xu, C., & Wang, W. G. (2014). Achieving high-efficiency hydrogen production using planar solid-oxide electrolysis stacks. *International Journal of Hydrogen Energy, 39*(21), 10833-10842.

Manage, M. N., Hodgson, D., Milligan, N., Simons, S. J. R., & Brett, D. J. L. (2011). A techno-economic appraisal of hydrogen generation and the case for solid oxide electrolyser cells. *International Journal of Hydrogen Energy, 36*(10), 5782-5796.

Martinez-Frias, J., Pham, A.-Q., & M. Aceves, S. (2003). A natural gas-assisted steam electrolyzer for high-efficiency production of hydrogen. *International Journal of Hydrogen Energy, 28*(5), 483-490.

Millet, P., & Grigoriev, S. (2013). Chapter 2 - Water Electrolysis Technologies. In L. M. G. A. M. Diéguez (Ed.), *Renewable Hydrogen Technologies* (pp. 19-41). Amsterdam: Elsevier.

Mingyi, L., Bo, Y., Jingming, X., & Jing, C. (2008). Thermodynamic analysis of the efficiency of high-temperature steam electrolysis system for hydrogen production. *Journal of Power Sources, 177*(2), 493-499.

Moriarty, P., & Honnery, D. (2009). Hydrogen's role in an uncertain energy future. *International Journal of Hydrogen Energy, 34*(1), 31-39.

National Renewable Energy Laboratory (NREL). (2011). *Hydrogen Production Cost Estimate Using Biomass Gasification*: U.S. Department of Energy Hydrogen and Fuel Cells Program.

Ni, M. (2012). An electrochemical model for syngas production by co-electrolysis of H2O and CO2. *Journal of Power Sources, 202*(0), 209-216.

Ni, M., Leung, M. K., & Leung, D. Y. (2008). Technological development of hydrogen production by solid oxide electrolyzer cell (SOEC). *International Journal of Hydrogen Energy, 33*(9), 2337-2354.

Ni, M., Leung, M. K. H., & Leung, D. Y. C. (2006). A modeling study on concentration overpotentials of a reversible solid oxide fuel cell. *Journal of Power Sources, 163*(1), 460-466.

Ni, M., Leung, M. K. H., & Leung, D. Y. C. (2007a). Energy and exergy analysis of hydrogen production by solid oxide steam electrolyzer plant. *International Journal of Hydrogen Energy, 32*(18), 4648-4660.

Ni, M., Leung, M. K. H., & Leung, D. Y. C. (2007b). Parametric study of solid oxide steam electrolyzer for hydrogen production. *International Journal of Hydrogen Energy, 32*(13), 2305-2313.

Noren, D. A., & Hoffman, M. A. (2005). Clarifying the Butler–Volmer equation and related approximations for calculating activation losses in solid oxide fuel cell models. *Journal of Power Sources, 152*(0), 175-181.

Reid, R. C., Prausnitz, J. M., & Poling, B. E. (1987). *The Properties of Gases and Liquids*. New York: McGraw-Hill.

Seo, Y. S., Shirley, A., & Kolaczkowski, S. T. (2002). Evaluation of thermodynamically favourable operating conditions for production of hydrogen in three different reforming technologies. *Journal of Power Sources, 108*(1–2), 213-225.

Shao, L., Wang, S., Qian, J., Ye, X., & Wen, T. (2013). Optimization of the electrode-supported tubular solid oxide cells for application on fuel cell and steam electrolysis. *International Journal of Hydrogen Energy, 38*(11), 4272-4280.

Smith Jr, R. L., Adschiri, T., & Arai, K. (2002). Energy integration of methane's partial-oxidation in supercritical water and exergy analysis. *Applied Energy, 71*(3), 205-214.

Stempien, J. P., Sun, Q., & Chan, S. H. (2013). Solid Oxide Electrolyzer Cell Modeling: A Review. *Journal of Power Technologies, 93*(4), 216-246.

Stoots, C., O'Brien, J., Condie, K., Herring, J., & Hartvigsen, J. (2008). *Initial Operation of the High-Temperature Electrolysis Integrated Laboratory Scale Experiment at INL.* Paper presented at the 2008 International Congress on Advances in Nuclear Power Plants.

Tsatsaronis, G. (2007). Definitions and nomenclature in exergy analysis and exergoeconomics. *Energy, 32*(4), 249-253.

Todd, B., & Young, J. (2002). Thermodynamic and transport properties of gases for use in solid oxide fuel cell modelling. *Journal of Power Sources, 110*(1), 186-200.

Udagawa, J., Aguiar, P., & Brandon, N. P. (2007). Hydrogen production through steam electrolysis: Model-based steady state performance of a cathode-supported intermediate temperature solid oxide electrolysis cell. *Journal of Power Sources, 166*(1), 127-136.

Udagawa, J., Aguiar, P., & Brandon, N. P. (2008). Hydrogen production through steam electrolysis: Control strategies for a cathode-supported intermediate temperature solid oxide electrolysis cell. *Journal of Power Sources, 180*(1), 354-364.

Welaya, Y. M. A., El Gohary, M. M., & Ammar, N. R. (2012). Steam and partial oxidation reforming options for hydrogen production from fossil fuels for PEM fuel cells. *Alexandria Engineering Journal, 51*(2), 69-75.

Xu, Y., Dai, Z., Li, C., Li, X., Zhou, Z., Yu, G., & Wang, F. (2014). Numerical simulation of natural gas non-catalytic partial oxidation reformer. *International Journal of Hydrogen Energy, 39*(17), 9149-9157.

Zhang, H., Lin, G., & Chen, J. (2010). Evaluation and calculation on the efficiency of a water electrolysis system for hydrogen production. *International Journal of Hydrogen Energy, 35*(20), 10851-10858.

Zhang, H., Su, S., Chen, X., Lin, G., & Chen, J. (2013). Configuration design and performance optimum analysis of a solar-driven high temperature steam electrolysis system for hydrogen production. *International Journal of Hydrogen Energy, 38*(11), 4298-4307.

Zhang, W., Croiset, E., Douglas, P., Fowler, M., & Entchev, E. (2005). Simulation of a tubular solid oxide fuel cell stack using AspenPlus TM unit operation models. *Energy Conversion and Management, 46*(2), 181-196.

Zhang, X., O'Brien, J. E., O'Brien, R. C., & Housley, G. K. (2013). Durability evaluation of reversible solid oxide cells. *Journal of Power Sources, 242*, 566-574.

APPENDIX

Appendix 1 Stream Result

Table A.1 Stream result

Stream	**1**	**2**	**3**
Temperature (K)	298.15	298.15	427.00
Pressure (atm)	1	5	5
Vapor fraction	0	0	1
Molar flow rate (kmol/hr)	5.70	5.70	5.70
Molar fraction			
Hydrogen	0.000	0.000	0.000
Water/Steam	1.000	1.000	1.000
Oxygen	0.000	0.000	0.000
Methane	0.000	0.000	0.000
Carbon dioxide	0.000	0.000	0.000
Carbon monoxide	0.000	0.000	0.000
Stream	**4**	**5**	**6**
Temperature (K)	427.00	427.00	1166.00
Pressure (atm)	5	5	5
Vapor fraction	1	1	1
Molar flow rate (kmol/hr)	0.70	5.00	5.00
Molar fraction			
Hydrogen	0.000	0.000	0.000
Water/Steam	1.000	1.000	1.000
Oxygen	0.000	0.000	0.000
Methane	0.000	0.000	0.000
Carbon dioxide	0.000	0.000	0.000
Carbon monoxide	0.000	0.000	0.000

Table A.1 Stream result (Continue)

Stream	**7**	**8**	**9**
Temperature (K)	1182.46	298.15	529.57
Pressure (atm)	5	1	5
Vapor fraction	1	1	1
Molar flow rate (kmol/hr)	6.09	5.00	5.00
Molar fraction			
Hydrogen	0.100	0.000	0.000
Water/Steam	0.900	0.000	0.000
Oxygen	0.000	1.000	1.000
Methane	0.000	0.000	0.000
Carbon dioxide	0.000	0.000	0.000
Carbon monoxide	0.000	0.000	0.000
Stream	**10**	**11**	**12**
Temperature (K)	1272.00	1273.00	1273.00
Pressure (atm)	5	5	5
Vapor fraction	1	1	1
Molar flow rate (kmol/hr)	5.00	7.49	5.00
Molar fraction			
Hydrogen	0.000	0.455	0.000
Water/Steam	0.000	0.358	0.000
Oxygen	1.000	0.189	1.000
Methane	0.000	0.000	0.000
Carbon dioxide	0.000	0.000	0.000
Carbon monoxide	0.000	0.000	0.000

Table A.1 Stream result (Continue)

Stream	**13**	**14**	**15**
Temperature (K)	1273.00	1273.00	1273.00
Pressure (atm)	5	5	5
Vapor fraction	1	1	1
Molar flow rate (kmol/hr)	6.09	1.09	5.00
Molar fraction			
Hydrogen	0.560	0.560	0.560
Water/Steam	0.440	0.440	0.440
Oxygen	0.000	0.000	0.000
Methane	0.000	0.000	0.000
Carbon dioxide	0.000	0.000	0.000
Carbon monoxide	0.000	0.000	0.000
Stream	**16**	**17**	**18**
Temperature (K)	428.00	1273.00	1273.00
Pressure (atm)	5	5	5
Vapor fraction	1	1	1
Molar flow rate (kmol/hr)	5.00	1.40	6.40
Molar fraction			
Hydrogen	0.560	0.000	0.000
Water/Steam	0.440	0.000	0.000
Oxygen	0.000	1.000	1.000
Methane	0.000	0.000	0.000
Carbon dioxide	0.000	0.000	0.000
Carbon monoxide	0.000	0.000	0.000

Table A.1 Stream result (Continue)

Stream	**19**	**20**	**21**
Temperature (K)	702.36	370.00	370.00
Pressure (atm)	5	5	5
Vapor fraction	1	1	1
Molar flow rate (kmol/hr)	6.40	6.40	4.48
Molar fraction			
Hydrogen	0.000	0.000	0.000
Water/Steam	0.000	0.000	0.000
Oxygen	1.000	1.000	1.000
Methane	0.000	0.000	0.000
Carbon dioxide	0.000	0.000	0.000
Carbon monoxide	0.000	0.000	0.000
Stream	**22**	**23**	**24**
Temperature (K)	370.00	298.15	530.30
Pressure (atm)	5	1	1
Vapor fraction	1	1	1
Molar flow rate (kmol/hr)	1.92	6.93	6.93
Molar fraction			
Hydrogen	0.000	0.000	0.000
Water/Steam	0.000	0.000	0.000
Oxygen	1.000	0.000	0.000
Methane	0.000	1.000	1.000
Carbon dioxide	0.000	0.000	0.000
Carbon monoxide	0.000	0.000	0.000

Table A.1 Stream result (Continue)

Stream	**25**	**26**
Temperature (K)	719.102	1373.00
Pressure (atm)	5	5
Vapor fraction	1	1
Molar flow rate (kmol/hr)	12.10	21.46
Molar fraction		
Hydrogen	0.000	0.576
Water/Steam	0.057	0.102
Oxygen	0.370	0.000
Methane	0.573	0.000
Carbon dioxide	0.000	0.025
Carbon monoxide	0.000	0.297

Appendix 2 Energy result

Table A.2 Energy result

Unit Operation	**Energy (kW)**
Steam generator	
Pump	0.035
Heater1	69.410
Solid oxide electrolysis cell	
Power stream	129.714
QOVP stream	6.574
QA	-0.0499
Partial oxidation reactor (POX stream)	64.187
Compressor 1	9.720
Compressor 2	35.353

VITA

Mr. Nuttawut Visitdumrongkul was born on August 12, 1990, in Phetchaburi, Thailand. He finished high school from Prommanusorn Phetchaburi, Phetchaburi in 2009. He received his Bachelor's Degree in Chemical Engineering from Srinakharinwirot University in 2013. He continued his graduate study at the Control and System Engineering Research Center, Department of Chemical Engineering, Chulalongkorn University and received the Master degree in 2015