

Solid Oxide Fuel Cell Integrated with Supercritical Water Oxidation Fueled by Ethanol

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Abstract

As solid oxide fuel cell (SOFC) can offer the widest potential variety of applications and high system efficiency, this study focused on the electricity generation in SOFC integrated with ethanol supercritical water oxidation. A thermodynamic model based on minimum free energy has been carried out. Because the effect of operating pressure from atmosphere to supercritical water was investigated, thermodynamic equilibrium based on the Peng-Robinson equation of state was used. The effects of reaction temperature, and amount of water and oxygen fed in supercritical water reactor on the heat required supplying reactor and the SOFC power generation have been reported. Results showed that the electricity generation of SOFC increased as the steam-to-ethanol ratio and reactor temperature increased because of the increase of hydrogen fed into the fuel cell but the hydrogen peroxide-to-ethanol ratio decreased. Although the increase of steam-to-ethanol ratio and reactor temperature increased hydrogen production, the total heat duty also increased. On the other hand, the reactor heat duty can be decreased by adding oxygen into the reactor because of the increase of exothermic energy.

Keywords: solid oxide fuel cell, supercritical water oxidation, steam reforming

1. Introduction

Among many different options of power generation, the most efficient and environmentally excellent method for electric power generation is a fuel cell. A solid oxide fuel cell (SOFC) is remarkably interesting because of its high operating temperature (ca. 1000 °C) such a high temperature allows use of non-noble catalysts, which have reasonable cost and are insensitive to certain fuel contaminants

[1]. In a fuel cell, the fuel, hydrogen, is electrochemically reacted with oxygen from air to produce electricity and usable heat. Among renewable sources, ethanol is a promising candidate since it is easily produced by biomass fermentation and has relatively high hydrogen content. Ethanol is also non-toxic and easy to store and transport.

In this study, supercritical water oxidation (SCWO) has received attention

due to an excellent reaction medium of SCW [2-3], although hydrogen can normally be produced by steam reforming, partial oxidation and oxidative steam reforming. The product gas is produced at a high pressure of more than 22.1 MPa, which is an advantage for high pressure hydrogen storage. The mixture of hydrogen, carbon dioxide, carbon monoxide and methane is a major product gas which can be fuel for SOFC. The use of a SOFC has an advantage because SOFC can not be poisoned by CO that makes it highly fuel-flexible.

So far, various researches on thermodynamic analysis of biomass gasification for hydrogen production in SCW at temperatures and pressures above the critical point of water of 374°C and 22.1 MPa have been performed [4-8]. But the work on thermodynamic analysis of ethanol supercritical water oxidation is limited. Thermodynamic analysis is very useful in providing theoretical guidance for optimization of design and operation of an ethanol supercritical water oxidation unit and fuel cell integrated system. Most researchers [4-6] carried out chemical equilibrium analysis of hydrogen production from biomass gasification in SCW based on Gibbs free energy minimization. Ioannides [9] focused on thermodynamic analysis of ethanol processors incorporating either a steam reformer or a partial oxidation reactor connected to water gas-shift and CO oxidation reactors for solid polymer fuel cell applications.

Previous study has included a study on the power generation through integrated steam reformer and SOFC system [10] and the combination of internal reforming SOFC and gas turbine [11]. Srisiriwat et al. [12] performed thermodynamic analysis of hydrogen production from ethanol in three different technologies, namely steam reforming (SR), partial oxidation (POX), and autothermal reforming (ATR).

In this study, system integration of ethanol SCWO reactor and SOFC has been

studied. The effect of operating conditions on the heat duty of the system and the power generation was also reported. The chemical equilibrium analysis of hydrogen production from ethanol in SCWO was investigated by using AspenPlus™.

2. Methodology

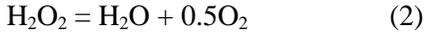
The schematic diagram of system integration of SCW reactor and SOFC is presented in Figure 1. The system consists of a steam generator, two vaporizers for ethanol and hydrogen peroxide, a preheater, a SCWO reactor, a high pressure hydrogen tank and SOFC. Hydrogen rich gas required for the anode side of the SOFC is produced from ethanol in a processor unit. In this study, AspenPlus™, commercially available software, was used for the thermodynamic calculation. The equilibrium compositions were calculated when operating conditions were input to the simulation. The Peng-Robinson equation of state, widely used in the field of supercritical fluids [6], was used for supercritical water conditions to explain the thermodynamic property of each species. The minimization of the Gibbs free energy was applied to determine the equilibrium compositions without specification of the reactions taking place in the system by using a RGIBBS reactor model. Existing unit operation models were combined with mathematical programs to calculate the electrical power and efficiency. Gibbs free energy function G of a system consisting of N species, with fixed T and P , can be expressed as a linear combination of chemical potential of each component in the system:

$$G = \sum_{i=1}^N n_i \mu_i = \sum_{i=1}^N n_i \mu_i^o + RT \sum_{i=1}^N n_i \ln f_i \quad (1)$$

where n_i is the moles of species i , μ_i the chemical potential, μ_i^o the chemical potential in standard state, R the molar gas

constant, T the temperature of system, and f_i partial fugacity.

In the SCWO reaction, the oxidant was hydrogen peroxide (H_2O_2) which completely decomposed into oxygen and water by thermal decomposition according to



This research studied the effect of steam-to-ethanol (S:E) molar ratio and hydrogen peroxide-to-ethanol (H:E) molar ratio based on the feedstock of 1 mol/sec of ethanol. The S:E molar ratio and H:E molar ratio parameters can be defined by:

$$S:E = \frac{\text{molar flow rate of } H_2O}{\text{molar flow rate of } C_2H_6O} \quad (3)$$

$$H:E = \frac{\text{molar flow rate of } H_2O_2}{\text{molar flow rate of } C_2H_6O} \quad (4)$$

It is noted that the S:E molar ratio excludes water produced from decomposition of H_2O_2 .

The main objective was to investigate the hydrogen production from the ethanol SCWO that was fed into the SOFC to produce electrical power.

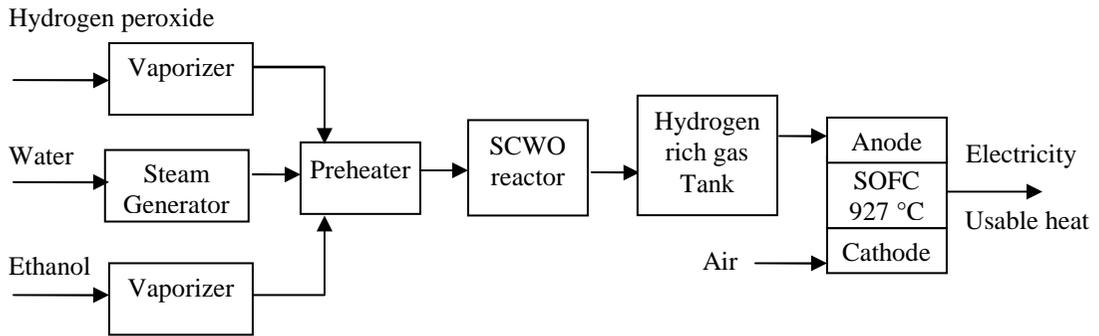


Fig. 1 Schematic diagram of SOFC integrated with ethanol supercritical water oxidation system.

For the calculation of the emf distribution along the channel, it was supposed that the oxygen anions flux through the electrolyte was uniform. As was demonstrated this assumption is true for multi-cell SOFCs. Emf was then calculated by the Nernst equation [14]

$$E = \frac{RT}{4F} \ln \frac{p_{O_2(c)} p_{H_2(a)}^2}{p_{H_2O(a)}^2} \quad (5)$$

where, R represents the universal gas constant, T the absolute temperature, F the Faraday's constant (96,484 J/mol V) and "a" and "c" stand for anode and cathode, respectively. It is supposed that the cathode

side of SOFC is fed by air and therefore $p_{O_2(c)} = 0.209$. Furthermore, the average emf of a multi-cell SOFC stack was defined as [15]

$$\bar{E} = \frac{1}{L} \int_0^L E(x) dx \quad (6)$$

where $x = x^*/L$ represents an independent dimensionless spatial variable and L is the length of the multi-cell anode channel.

The total current can be calculated by:

$$I = 2Fn_{H_2, react} \quad (7)$$

The cell power output is:

$$P_{SOFC} = \bar{E} \cdot I \quad (8)$$

Finally, the electrical efficiency [15] of the SOFC is calculated by:

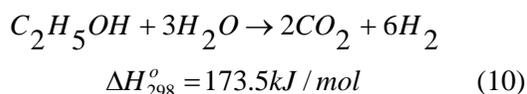
$$\eta_{el,SOFC} = \frac{\bar{E} \cdot I}{n_{EtOH,in} \cdot LHV_{EtOH}} \quad (9)$$

where LHV_{EtOH} the lower heating value of ethanol (1235 kJ/mole of ethanol).

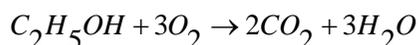
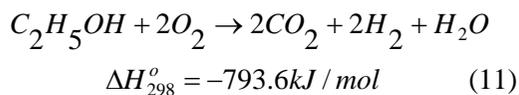
In this study, the effects of operating conditions, reactor temperature, amount of water and oxygen, and pressure, on the hydrogen production and electricity generation from SOFC were studied. Moreover, the heat required for the reactor and the total energy consumptions were calculated as the total heat including all heaters and the SCWO reactor.

3. Results and Discussion

The stoichiometry of the endothermic reaction of ethanol steam reforming for the maximum hydrogen production can be defined by



Normally, in both thermodynamic analysis and experimental study, the stoichiometric coefficient of hydrogen can not reach 6 because in the steam reforming conditions other competing reactions, both exothermic and endothermic, take place such as ethanol decomposition and dehydrogenation to produce methane and carbon monoxide. In the presence of oxygen in reactor, the ethanol oxidations can be presented:



$$\Delta H_{298}^{\circ} = -1277.2 \text{ kJ/mol} \quad (12)$$

Moreover, the reverse water gas-shift and methanation reactions also take place in the system [16].

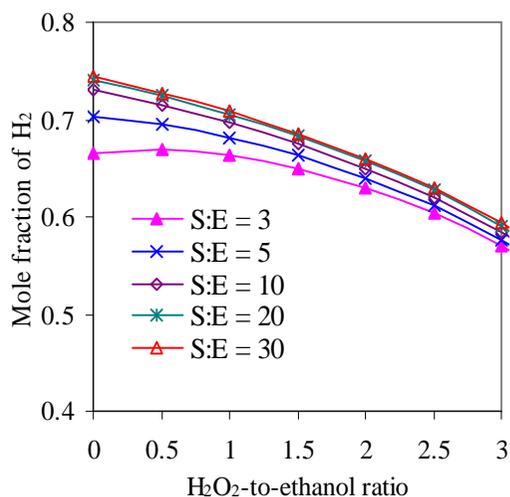
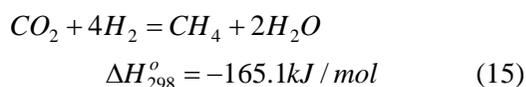
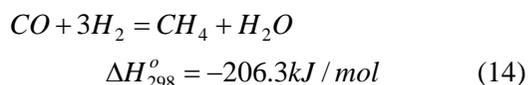
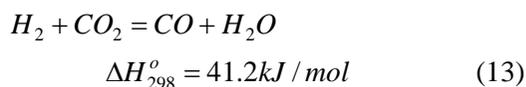


Fig. 2 Effect of S:E ratio and H:E ratio on mole fraction of H_2 at 650 °C and 0.1 MPa.

Figure 2 shows, under atmospheric pressure, the effect of S:E ratio and H:E ratio on mole fraction of hydrogen based on dry gas composition. Hydrogen continuously decreased as H:E ratio increased but it increased with increasing S:E ratio. However, the increase of S:E ratio also increased the endothermic heat of the reactor resulting in an increase of total energy as shown in Figures 3 and 4 because of the higher energy required by the

endothermic reaction. The positive and negative values of heat load mean endothermic and exothermic reactions that also require respectively a heat source and a heat sink. On the other hand, the increase of hydrogen peroxide, decomposed to oxygen, decreased the heat duty of reactor because of the exothermic reaction. Although hydrogen increased as S:E increased, the energy consumption also increased; it means that hydrogen was consumed to produce electricity in SOFC and also used to supply the total heat required in the system.

At SCW conditions, the effect of reactor temperature, S:E ratio and H:E ratio on hydrogen production and heat load has also been investigated. Figure 5 shows the increase of hydrogen with increasing S:E ratio and reactor temperature. The heat required by SCW reactor increased as the S:E ratio and temperature increased as shown in Figure 6. In this study, we were interested in the zone of neutral energy where heat supplied and used in the reactor was balanced so that hot and cold utilities were not necessary.

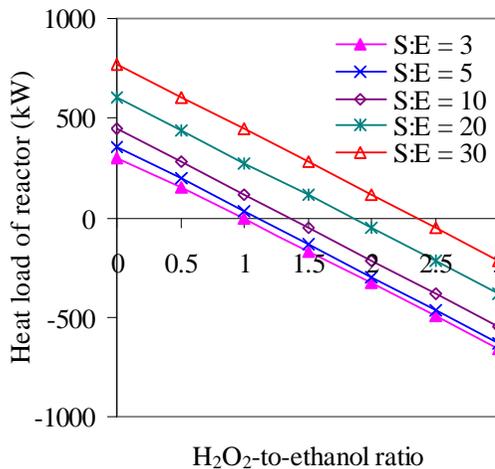


Fig. 3 Effect of S:E ratio and H:E ratio on heat load of reactor at 650 °C and 0.1 MPa.

Figure 7 shows that the increase of H:E ratio decreased mole fraction of hydrogen because of oxidation reaction but H:E ratio only slightly affected the mole fraction of hydrogen when temperature was lower than 700 °C.

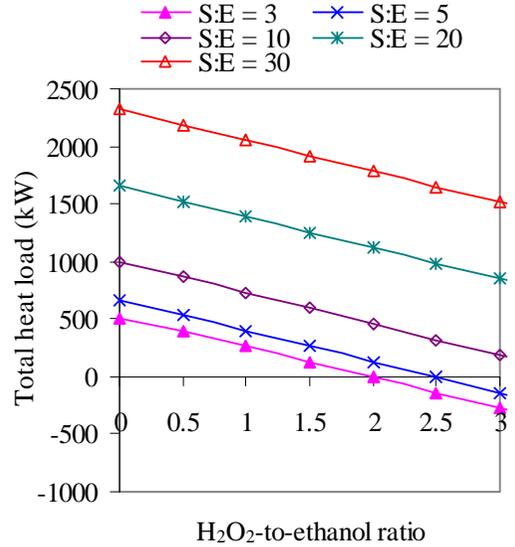


Fig. 4 Effect of S:E ratio and H:E ratio on total heat load of reactor at 650 °C and 0.1 MPa.

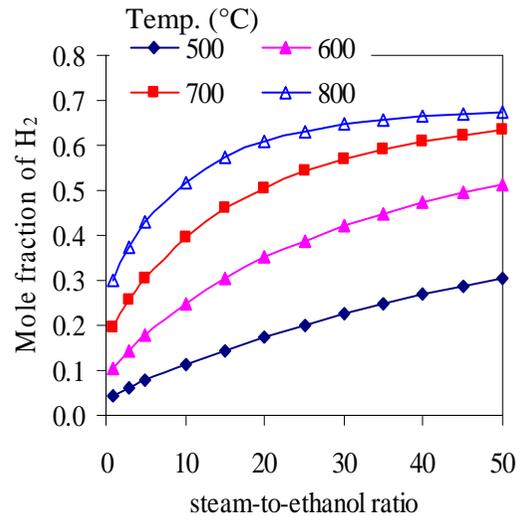


Fig. 5 Effect of temperature and S:E ratio on mole fraction of H₂ at H:E = 1.5 and 25.0 MPa.

The heat required by the SCW reactor decreased as H:E ratio increased as shown in Figure 8 because of the increase of exothermic energy in the reactor. The effect of reactor temperature and S:E ratio on the total heat duty was also presented in Figure 9. The neutral energy state appeared when S:E ratio was lower than 5 in the temperature range between 500 – 800 °C and H:E ratio of 1.5. However, the low S:E ratio gave the low SOFC power generation as shown in Figure 10.

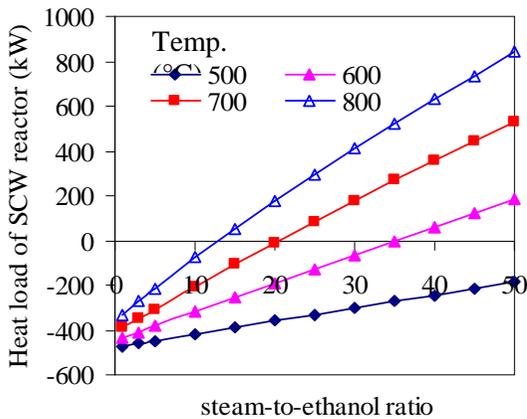


Fig. 6 Effect of temperature and S:E ratio on heat load of SCW reactor at H:E = 1.5 and 25.0 MPa.

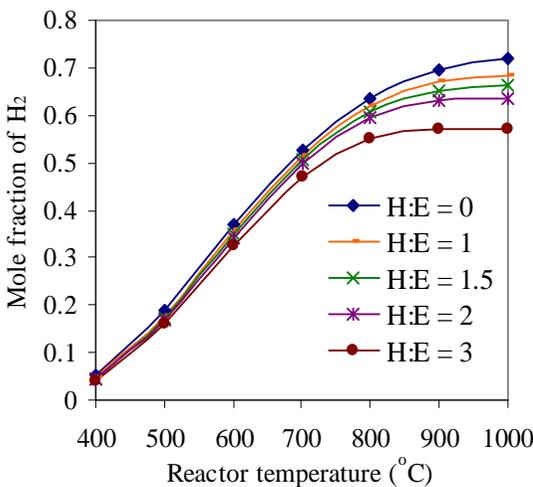


Fig. 7 Effect of temperature and H:E ratio on mole fraction of H₂ at S:E = 20 and 25.0 MPa.

The electrical power increased with increasing S:E ratio and reactor temperature although the total energy required increased. At the SCW conditions, when S:E ratio of 20, H:E ratio of 1.5 and reactor temperature of 800 °C was studied, the SOFC power generation and the electrical efficiency were approximately 420 kW and 34 %, respectively. The result showed that SOFC power generation at SCW conditions was less than that at atmospheric conditions because of lower hydrogen yield. Srisiriwat [11] concluded that, in the case of S:E ratio of 4 and 700 °C of reactor temperature, the SOFC power generation and electrical efficiency was 756.4 kW and 61% for atmospheric operation. Although atmospheric pressure gave higher electrical power than SCW conditions, the atmospheric pressure required higher total heat input to the system than SCW conditions.

Normally, the high temperature SOFC reaction produced exothermic energy that could be used to supply heat to the vaporizers and reactors in the system. Srisiriwat [10-11] showed that, at atmospheric conditions with S:E ratio of 10 and reactor temperature of 700 °C, the hot stream from SOFC provided enough heat in the heat exchangers and the cold utility could be reduced by combined SOFC and gas turbine operation when heat integration was considered. Therefore, heat integration of SOFC integrated with SCWO fed by ethanol will be further investigated.

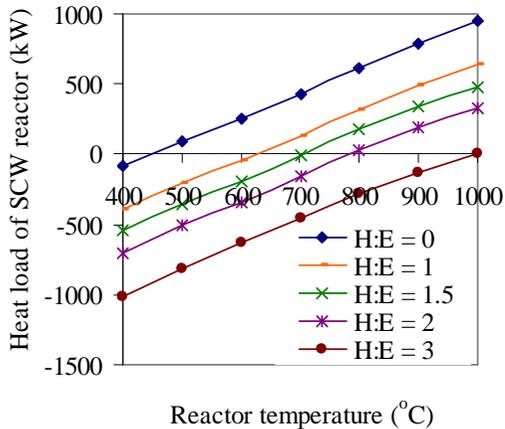


Fig. 8: Effect of temperature and H:E ratio on heat load of SCW reactor at S:E = 20 and 25.0 MPa.

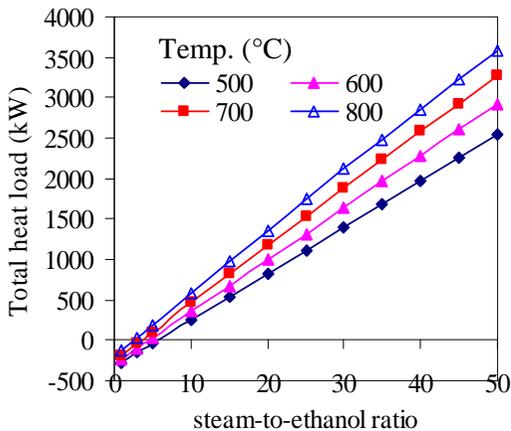


Fig. 9: Effect of temperature and S:E ratio on total heat load of SCW reactor at H:E = 1.5 and 25.0 MPa.

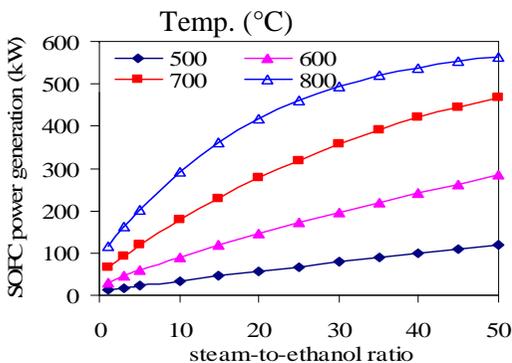


Fig. 10 Effect of temperature and S:E ratio on SOFC power generation at H:E = 1.5 and 25.0 MPa.

4. Conclusion

The system of SOFC integrated with SCWO fueled by ethanol has been investigated. The hydrogen mole fraction on a dry basis and endothermic heat of the SCW reactor increased rapidly with increasing S:E ratio and reaction temperature but decreased with increasing presence of oxygen decomposed from hydrogen peroxide. The power generation and electrical efficiency increased with increasing S:E ratio and reactor temperature although the total energy required increased.

5. Acknowledgement

Financial support from Pathumwan Institute of Technology is gratefully acknowledged. Special mention should be made to Chemical Engineering Practice School, King Mongkut's University of Technology Thonburi for supporting AspenPlus™ program.

6. References

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