Optimization of Biogas-Fed Reversible Solid Oxide Fuel Cell System

W Mungkalasiri\textsuperscript{1} and J Mungkalasiri\textsuperscript{2}

\textsuperscript{1} Engineering Faculty, Thammasat University, Thailand
\textsuperscript{2} TIIS, National Science and Technology Development Agency, Thailand
E-mail: pworanee@engr.tu.ac.th

Abstract. In this work, an integrated system of biogas tri-reforming and solid oxide fuel cell (SOFC) for power generation was studied by using Aspen Plus simulation. Biogas obtained from a sugar industry with 75\%CH\textsubscript{4} and 25\%CO\textsubscript{2} was used as feedstock. However, biogas-feed SOFC power generation system released carbon dioxide (CO\textsubscript{2}) which was the main cause of global warming. Therefore, solid oxide electrolysis cell (SOEC) was considered for CO\textsubscript{2} reduction called reversible solid oxide fuel cell (RSOFC). The RSOFC system included four units; tri-reforming, SOFC, SOEC and methanation. This research aimed to optimize operating conditions of the RSOFC system for generating maximum electricity and reducing CO\textsubscript{2}. The results of biogas tri-reforming with SOFC system showed that the electrical power production was 6233 W/m\textsuperscript{2} and CO\textsubscript{2} emission was 1603 kg/hr. The results of RSOFC system indicated that CO\textsubscript{2} emission was reduced by 24.7\%.

1. Introduction
Fuel cell has received significant attention as a clean and efficient energy conversion technology. Solid oxide fuel cells (SOFC) are the most efficient fuel cell electricity generators, flexible in the choice of fuel such as carbon-based fuel like natural gas, biogas [1]. Biogas is produced by municipal solid waste landfills, sludge digester in wastewater treatment plants. Biogas is mainly composed by methane (CH\textsubscript{4}) and carbon dioxide (CO\textsubscript{2}). The suitable pathway to produce hydrogen from biogas is a reforming method [2]. However, using carbon-based fuel in a reforming with fuel cell power generation system, carbon dioxide (CO\textsubscript{2}) is produced which cause global warming effect. One alternative to reduce the CO\textsubscript{2} while producing valuable syngas is the use of an electrolyzer as solid oxide electrolysis cell (SOEC). The electrolysis cell uses a renewable energy supply such as solar, wind, hydro to produce hydrogen from H\textsubscript{2}O and CO\textsubscript{2} [3]. Reversible solid oxide fuel cell (RSOFC) is a device that can operates using 2 modes: fuel cell mode and electrolysis mode. In the fuel cell mode, electricity is generated by electrochemical reaction of a fuel such as hydrogen, hydrocarbons, alcohols, etc. with air/oxygen. In the electrolysis mode, a solid oxide electrolysis cell or SOEC produces hydrogen from water or mixtures of water and carbon dioxide [4].

The objective of this work was to optimize RSOFC operating conditions for generating the maximum electricity and reducing CO\textsubscript{2} emission. In addition, a comparative study of tri-reforming with SOFC system and RSOFC system performance was evaluated. In this study, power generation system was modelled via Aspen Plus program.
2. Theory

2.1. Tri-reforming process
Biogas is fed to a tri-reforming producing hydrogen. The tri-reforming process consists of dry reforming (DR), steam reforming (SR) and partial oxidation (POX). Besides, the water-gas shift reaction (WGS) can also occur. The reactions are [1]

\[
\begin{align*}
\text{DR:} & \quad \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2 & \Delta H^0 &= 247.3 \text{ kJ/mol} \\
\text{SR:} & \quad \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 & \Delta H^0 &= 206.3 \text{ kJ/mol} \\
\text{POX:} & \quad \text{CH}_4 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{CO} + 2\text{H}_2 & \Delta H^0 &= -35.6 \text{ kJ/mol} \\
\text{WGS:} & \quad \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 & \Delta H^0 &= -41.9 \text{ kJ/mol}
\end{align*}
\]

2.2. Solid oxide fuel cell (SOFC)
The electrochemical reactions involved in a solid oxide fuel cell are [1]
\[
\begin{align*}
\text{Anode:} & \quad \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \\
\text{Cathode:} & \quad \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-} \\
\text{Overall:} & \quad \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}
\end{align*}
\]

2.3. Solid oxide electrolysis cell (SOEC)
SOEC performance depends on the reaction rates, operating conditions, supply of electricity. The net reactions are [4]
\[
\begin{align*}
\text{Cathode:} & \quad \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{O}^{2-} \\
& \quad \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO} + \text{O}^{2-} \\
\text{Anode:} & \quad \text{O}^{2-} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{e}^- \\
\text{Overall:} & \quad \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2 + \text{CO} + \text{O}_2
\end{align*}
\]

SOEC system is analyzed by an electrochemistry model [5]

2.4. Methanation process
Renewable electrical energy can be stored as chemical energy. An advantage of storage is the higher density of methane. The main conversion step is the methanation. The carbon monoxide (CO) methanation reaction is [3]
\[
\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H^0 = -206.28 \text{ kJ/mol}
\]

In addition, water gas shift reaction occurs simultaneously
\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^0 = -41.16 \text{ kJ/mol}
\]

3. Methodology
The RSOFC system included four unit processes as shown in figure 1. The tri-reforming, SOFC, SOEC and methanation processes were performed by Aspen Plus v.9.0 simulation program. In this study, biogas from a sugar industry contained 75%CH\textsubscript{4} and 25%CO\textsubscript{2} was used as feedstock with flowrate of 36.42 mol/hr [3]. The effect of several parameters such as reforming temperature (200–1200°C), H\textsubscript{2}O/CH\textsubscript{4} ratio (0.1-3.0), O\textsubscript{2}/CH\textsubscript{4} ratio (0.1-1.0) [6], SOFC temperature (800-1000°C) [7], SOEC temperature (500-1000°C) [3], methanation temperature (140-500°C) and methanation pressure (1-20 bar) on power generation were investigated [8].

![Image](image.png)

**Figure 1.** Reversible solid oxide fuel cell (RSOFC) system.
4. Results
Biogas from the sugar factory wastewater was fed with water and air into the tri-forming process producing hydrogen. Then, the gas was introduced to generate power by integrating the tri-reforming reaction with solid oxide fuel cell (SOFC) as shown in figure 2. However, an integrating tri-reforming with SOFC system released carbon dioxide (CO₂) which was the greenhouse gas that the main caused of global warming.

![Figure 2. Tri-reforming with SOFC system.](image)

Therefore, this study aimed to reduce carbon dioxide by using a solid oxide electrolysis cell (SOEC) with SOFC called a reversible solid oxide fuel cell (RSOFC). A SOEC was an electrochemical device able to produce hydrogen from water or SOFC syngas (mixtures of water and carbon dioxide). Electrical energy was required in the electrolyzer to produce energy (hydrogen). The methanation process was operated with SOEC as power-to-gas to produce methane (CH₄) as energy storage. Then, CH₄ was used as a fuel of tri-reforming process as shown in figure 1.

In this work, the simulation of RSOFC system was studied to optimized operating conditions for maximum SOFC power output with low carbon dioxide emission.

4.1. Tri-reforming process
The effect of tri-reforming temperature was evaluated. The results revealed that the optimal operating temperature was 700°C because a large amount of hydrogen gas (H₂) was produced as shown in figure 3. However, at high temperature (higher than 700°C) hydrogen flowrate was decreased because of reverse water gas shift reaction. Thus, carbon monoxide (CO) was produced at high temperature operation.

![Figure 3. The effect of tri-reforming temperature on hydrogen production.](image)
The effect of \( \text{H}_2\text{O}/\text{CH}_4 \) ratio in tri-reforming process was evaluated. The results as shown in figure 4 revealed that higher \( \text{H}_2\text{O}/\text{CH}_4 \) ratio caused higher hydrogen product because of steam reforming and water gas shift reactions. However, when \( \text{H}_2\text{O}/\text{CH}_4 \) ratio was higher than 3, a large reactor size was required so operating cost and energy consumption were increased [2].

![Figure 4](image)

**Figure 4.** The effect of \( \text{H}_2\text{O}/\text{CH}_4 \) ratio on hydrogen production in tri-reforming process.

The effect of \( \text{O}_2/\text{CH}_4 \) ratio in tri-reforming process was evaluated. The results revealed that increasing \( \text{O}_2/\text{CH}_4 \) ratio caused decreasing hydrogen product as shown in figure 5 because of the partial oxidation reaction. At high amount of oxygen, combustion reaction occurred and produced \( \text{CO}_2 \) with steam. However, when \( \text{O}_2/\text{CH}_4 \) ratio was less than 0.1, tri-reforming process operation needed more energy consumption.

![Figure 5](image)

**Figure 5.** The effect of \( \text{O}_2/\text{CH}_4 \) ratio on hydrogen production in tri-reforming process.

### 4.2. Solid oxide fuel cell (SOFC)

The effect of SOFC temperature under atmospheric pressure was studied. The results revealed that optimal SOFC temperature was 1000°C as shown in figure 6. This was mainly caused by an increase in the open-circuit voltage and a decrease in the activation and ohmic overpotentials. Nevertheless, the high temperature operation of SOFC (>1000°C) offered many problems such as complicated operation and control, short stack life time and long start-up time [7]. In addition, carbon dioxide (\( \text{CO}_2 \)) was discharged that caused environmental problem.
4.3. Solid oxide electrolysis cell (SOEC)
The effect of SOEC temperature under atmospheric pressure was studied. The results revealed that at 500-800°C of SOEC temperature, higher temperature caused higher hydrogen mole flow. However, when temperature higher than 800°C the amount of hydrogen gas was relatively constant but the amount of carbon dioxide was continuously increased because of H$_2$O electrolysis reaction, CO$_2$ electrolysis reaction and reverse water gas shift reaction. Thus, the optimal operating temperature of SOEC was 800°C as shown in Figure 7.

4.4. Methanation process
Synthesis gas obtained from SOEC was fed to the methanation process to produce methane as energy storage. In addition, methane was a main feedstock of tri-reforming process. Therefore, methane from methanation process fed to tri-reforming process without additional methane or biogas. The methanation reaction in this system was carbon monoxide methanation reaction, which was an exothermic reaction. However, at high temperature operation a water gas shift reaction also occurred. Thus, when the temperature was increased, the amount of methane product reduced with increased amount of carbon dioxide (CO$_2$). The simulation results revealed that the optimal operating temperature of the methanation process was 350°C. Moreover, the influence of pressure was studied. It was found that increased pressure caused slightly higher methane. Thus, the optimal pressure of the methanation process was 1 bar.
4.5. RSOFC optimal operating conditions

From optimal operating conditions of the RSOFC system as shown in table 1, it was found that power density produced by SOFC was 6489.56 W/m² and CO₂ release rate was 1206.11 kg/hr. However, SOEC required a huge amount of power, so renewable energy sources such as solar energy, wind energy should be considered.

| Unit process          | Optimal operating conditions | Power density production (W/m²) |
|-----------------------|------------------------------|---------------------------------|
| Tri-reforming         | 700°C, 1 bar, 3:1 of H₂O/CH₄, 0.1:1 of O₂/CH₄ | 6489.56 |
| SOFC                  | 1000°C, 1 bar                |                                 |
| SOEC                  | 800°C, 1 bar                 |                                 |
| Methanation           | 350°C, 1 bar                 |                                 |

Furthermore, the proportion of carbon dioxide emission to power production from the RSOFC system was evaluated using 500 m² of SOFC active area [9]. The result was compared with other power generation system as shown in table 2. The result revealed that for 1 kWh of power generation, CO₂ discharged from the RSOFC system was 0.37 close to natural gas power plant which had lower greenhouse gas emission than coal and oil. While biogas-fed tri-reforming with SOFC system and coal power plant produced a large amount of CO₂ by 0.51 and 0.91, respectively.

| Power generation system | CO₂ emission per power (kgCO₂/kWh) |
|-------------------------|-------------------------------------|
| Tri-reforming with SOFC | 0.51                                |
| RSOF abc                 | 0.37                                |
| Coal power plant [10]   | 0.91                                |
| Natural gas power plant [10] | 0.39                            |

5. Conclusion

The objective of this work was optimizing RSOFC operating conditions for generating the maximum electricity and reducing CO₂ emission. Aspen Plus simulator was performed the RSOFC system. The results revealed that optimal operating conditions of tri-reforming process were 700°C of temperature with 3:1 of H₂O/CH₄ ratio and 0.1:1 of O₂/CH₄ ratio. In addition, optimal operating temperatures of SOFC, SOEC and methanation were 1000°C, 800°C and 350°C, respectively under atmospheric pressure. In RSOFC system, power production was 6489.56 W/m² with low CO₂ emission (0.37 kgCO₂/kWh) compared to tri-reforming with SOFC system (0.51 kgCO₂/kWh). However, RSOFC system required external source of power for electrolysis process. Thus, renewable energy sources should be considered for reduction of energy price.

6. References

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