

# Systematic Analysis of Proton Electrolyte Membrane Fuel Cell Systems Integrated with Biogas Reforming Process

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This study presents a thermodynamic analysis of a biogas reforming process and proton electrolyte membrane fuel cell (PEMFC) integrated process. Different biogas reforming processes considered are dry and steam reforming. The aim is to determine the optimal reforming process for hydrogen production from biogas in the PEMFC system. The formation of carbon is concerned in the hydrogen production. The simulation results show that increases in the steam-to-carbon ratio and reformer temperatures can improve the hydrogen yield and reduce the carbon formation. The steam reforming of biogas is a suitable hydrogen production process due to its lowest energy consumption and complete carbon elimination. The optimal operating conditions are temperature of 800 °C and steam-to-methane ratio (H<sub>2</sub>O/CH<sub>4</sub>) of one. From the performance analysis of the PEMFC system integrated with the suitable biogas reforming process, it is found that when the PEMFC is operated at high temperature, the efficiencies of the PEMFC and the overall system can be improved. The performance of the PEMFC system with the installation of a water gas shift membrane unit in the hydrogen purification step is slightly increased, compared with a conventional process, because the high pressure operation of the membrane unit requires high energy consumption.

## 1. Introduction

Due to the environmental concern, clean and sustainable energy becomes important for the future. Hydrogen is expected to be an alternative fuel because it is an environmentally friendly fuel with high combustion efficiency (Arpornwichanop et al., 2011). In general, hydrogen is mostly derived from the reforming process of natural gas, which is the non-renewable resource. Alternatively, the production of hydrogen from renewable energy sources is an interesting option.

Among the various types of the renewable sources, biogas is a potential fuel, which can be produced through an anaerobic digestion of organic material, such as biomass, municipal waste and sewage. Biogas mainly consists of methane and carbon dioxide and can be directly used as a combustible gas; however, the combustion process of biogas to generate useful heat is inefficient. In contrast, the utilization of biogas as feedstock for a reforming process to produce hydrogen offers several advantages; (i) it can reduce the emission of green house gas, (ii) it is a renewable fuel, which can replace the natural gas for hydrogen production and (iii) it is easily produced from available local agricultural products.

Since methane and carbon dioxide are the major components of biogas, carbon dioxide reforming or dry reforming of methane is an interesting method to convert biogas into hydrogen. This endothermic reaction requires high-temperature operation to increase the equilibrium conversion. In addition, a carbon formation, which causes the catalyst deactivation, is the serious problem of the dry reforming. An addition of steam to the reforming environment is an effective way to prevent the formation of carbon in the reforming process (Choudhary and Mondal, 2006). Therefore, the investigation of dry and steam reforming of biogas should be performed.

To date, a number of studies have been concentrated on the synthesis of catalysts to minimize the carbon formation and maximize the hydrogen yield (Kambolis et al., 2010). In addition, many investigations have been focused on the thermodynamic analyses of hydrogen production from various fuels using different reforming technologies. The aim was to determine optimal operating conditions, which not only maximizes the hydrogen product, but also minimizes the carbon formation. However, the theoretical analysis of the hydrogen production from biogas is still limited. This understanding would lead to the determination of a suitable reforming process of biogas.

In general, a synthesis gas (“syngas”) obtained from reforming processes consists of hydrogen and carbon monoxide (CO). Use of the syngas with high hydrogen content for the electricity generation based on a fuel cell technology has been received much attention. However, it is found that the syngas cannot be directly fed to a fuel cell, especially a low-temperature fuel cell like a proton electrolyte membrane fuel cell (PEMFC), due to the high content of carbon monoxide; this causes the deactivation of the anode catalyst. To overcome this problem, the syngas is treated by the two-step water gas shift (WGS) reactor: high-temperature and low-temperature water gas shift reactors (HT-WGS and LT-WGS). However, when the two-step WGS reactor is applied, the CO concentration still exceeds its limitation due to the equilibrium constraint of the exothermic reaction, which favours at the low-temperature operation. To further purify the syngas, other purification units are added to the fuel processing system. Among the various technologies to reduce the CO content, a preferential oxidation (PROX) process is a widely used method. However, this conventional method is technically more complex and requires high operating cost because the reaction and separation of the product stream are required in this hydrogen production process. Furthermore, a portion of hydrogen is also consumed by the hydrogen oxidation reaction.

The objective of this work is to investigate the performance of the integration system of a biogas processing, which consists of reforming and membrane-based water gas shift reactors, for hydrogen production, and a proton electrolyte membrane fuel cell (PEMFC) for power generation. The membrane water gas shift (MWGS) reactor is employed to improve the fuel processing step for pure hydrogen production. Simulation studies are performed using a process simulator. The thermodynamic analysis of production of hydrogen from biogas based on different reforming processes, i.e., dry reforming and steam reforming is carried out. Effect of the reforming operating conditions, including temperature, biogas composition and steam-to-methane ratio, on the hydrogen production and carbon formation is also considered to obtain the suitable biogas reforming process. The integration of the biogas processing unit and PEMFC for power generation is also studied.

## 2. Integrated biogas reforming and PEMFC system

The integrated biogas reforming and PEMFC system (Figure 1) consists of three main parts: (i) the biogas reforming process where biogas is converted into a synthesis gas, (ii) the hydrogen purification unit in which CO in the synthesis gas is reduced and (ii) the PEMFC where electricity is generated via the electrochemical reaction of hydrogen and oxygen.

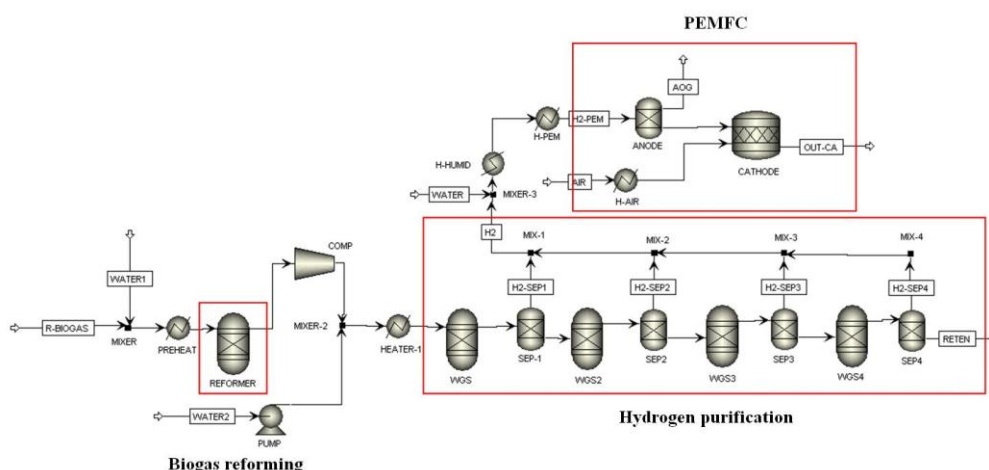


Figure 1: The integrated biogas reforming and PEMFC system.

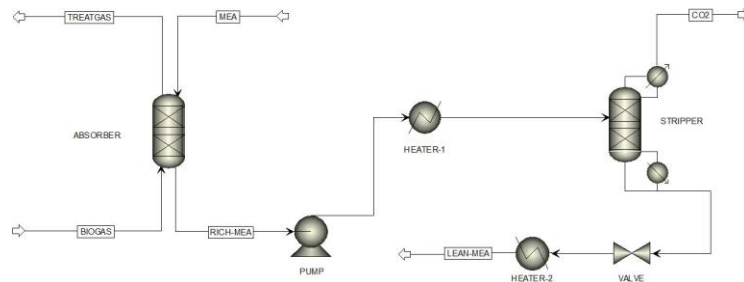


Figure 2: The biogas upgrading process.

Biogas and water are introduced to the PEMFC system at the temperature of 25 °C and pressure of 1 atm and then preheated to the temperature of 400 °C before they are fed to the reformer. Three different reforming methods are considered: dry reforming of biogas, steam reforming of biogas and steam reforming of upgraded biogas, which a portion of carbon dioxide is removed from biogas. The obtained synthesis gas is purified to reduce the CO content below the specified requirement for PEMFC operation (less than 10 ppm.). In this study, a water gas shift membrane-based processes is considered. Pure hydrogen obtained is used as fuel for running the PEMFC

### 2.1 Biogas reforming

The composition of the synthesis gas derived from the reformer is determined from a thermodynamic analysis, which is based on the minimization of Gibbs free energy. The reactor module, Rgibbs, in Aspen plus simulator is used to represent the reformer and the Peng-Robinson (PENG-ROB) model is employed to compute the thermodynamic properties. The chemical components involved the reforming of biogas are hydrogen, carbon dioxide, water, carbon monoxide and solid carbon.

For the steam reforming process of upgraded biogas, biogas is first sent to an absorption process using monoethanolamine (MEA) as a solvent, to remove carbon dioxide. Biogas with high methane fraction is then employed for the reforming process. Figure 2 shows the diagram of the biogas upgrading unit. In the absorber, carbon dioxide, weak acid gas, reacts with MEA, weak base, via the electrolyte reaction. The Electrolyte-NRTL (ELECRTL) model is used for simulation of the absorber. Table 1 shows operating conditions for the biogas upgrading process.

### 2.2 Hydrogen purification

In general, the synthesis gas obtained from the reforming process contains mostly hydrogen and CO. To avoid the CO poisoning problem in PEMFC and improve the PEMFC performance, high pure hydrogen is required. CO can be converted to more hydrogen through the water gas shift reaction. In this study, a water gas shift membrane reactor is applied for CO removal and pure hydrogen separation. The membrane reactor is modelled using a sequential modular of the reaction and separation sections (Ye et al., 2009); it is divided into the water gas shift sub-reformers and the membrane sub-separators, as can be seen from Figure 1. At each sub-reformer, the Rgibbs reactor model is used to simulate the water gas shift reaction, whereas the ideal separator model is used to represent the membrane separator. The amount of hydrogen that is separated by the separator is assumed to be 80% of the hydrogen derived from the reformer at the equilibrium condition (Lyubovsky et al., 2006).

### 2.3 PEMFC

The model of the PEMFC is divided into two parts: the anode and the cathode. The ideal separator is used to explain the anode where hydrogen in the synthesis gas is sent to the cathode side. The Rgibbs reactor represents the cathode where oxygen reacts with hydrogen via the electrochemical reaction to generate electricity. The output cell voltage of a single fuel cell ( $V_{cell}$ ) can be determined from the reversible cell voltage ( $E^{OCV}$ ) and the irreversible voltage losses, i.e., activation loss ( $V_{act}$ ), ohmic loss ( $V_{ohmic}$ ) and concentration loss ( $V_{conc}$ ), as shown in the following equation:

$$V_{cell} = E^{OCV} - V_{act} - V_{ohmic} - V_{conc} \quad (1)$$

Detail of the electrochemical models used to determine the reversible cell voltage and various voltage losses can be found in Francesconi et al. (2010). Table 2 shows the value of the model parameters used for simulations of the PEMFC.

Table 1: Operating conditions of the biogas upgrading process

ABSORBER	Model	Radfrac.
	Pressure (atm)	1
	Condenser type	-
	Reboiler type	-
	Number of stage	16
	MEA feed stage	16
	Biogas feed stage	1
STRIPPER	Model	Radfrac.
	Pressure (atm)	2
	Condenser type	-
	Reboiler type	Kettle
	Number of stage	16
PUMP	Type	Isentropic
	Outlet pressure	2
VALVE	Type	Adiabatic flash with the specified outlet pressure
	Outlet pressure	1
HEATER-1	Temperature (°C)	90
	Pressure (atm)	2
HEATER-2	Temperature (°C)	35
	Pressure (atm)	1

Table 2: Model parameters used for PEMFC simulation

$N_{\text{cell}}$	35	$\xi_3$	$7.6 \times 10^{-5}$
$A_{\text{cell}}(\text{cm}^2)$	232	$\xi_5$	$-1.93 \times 10^{-4}$
$L_m(\mu\text{m})$	178	$\psi$	23
$B(V)$	0.016	$i_{\text{max}}(\text{A}/\text{cm}^2)$	1.5
$R_{\text{elec}}(\Omega)$	0.0003	$i_n(\text{A}/\text{cm}^2)$	0.0012
$\xi_1$	-0.948		
$\xi_2$	$0.00286 + 0.0002 \ln(A_{\text{cell}}) + 4.3 \times 10^{-5} \ln(C_{\text{H}_2})$		

### 3. Results and discussion

#### 3.1 Dry reforming of biogas

In this section, the thermodynamic analysis of the dry reforming of biogas for hydrogen production is presented by considering the effect of key operating parameters. Figure 3(a) shows the effect of reformer temperatures on the equilibrium compositions of the synthesis gas product when biogas at the carbon dioxide-to-methane ratio ( $\text{CO}_2/\text{CH}_4$ ) of 0.5 is used as fuel. The result shows that  $\text{CH}_4$  and  $\text{CO}_2$  decrease with increasing reformer temperatures because of the endothermicity of the dry reforming reaction, which favors at high temperatures. Thus, the higher  $\text{H}_2$  and  $\text{CO}$  are observed. In addition, more carbon is generated at low temperatures due to the exothermic  $\text{CO}$  disproportionation and  $\text{CO}$  reduction reactions. Regarding the biogas composition, the results indicate (not shown in the figure) that when the fraction of

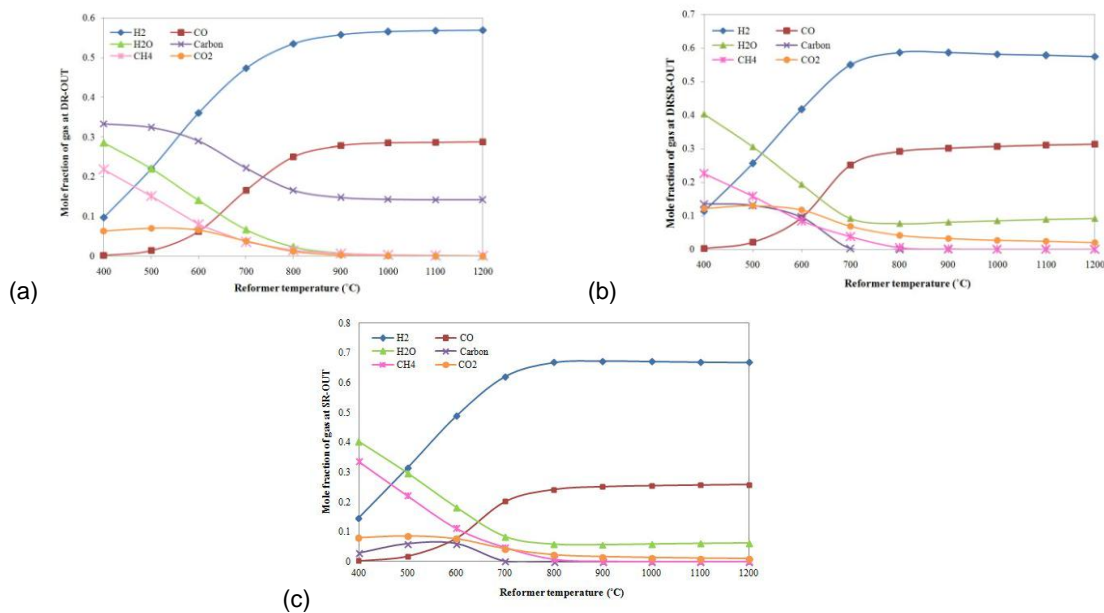


Figure 3: Effect of the reformer temperature on the composition of synthesis gas: (a) dry reforming of biogas ( $CO_2/CH_4 = 0.5$ ), (b) steam reforming of biogas ( $CO_2/CH_4 = 0.5$  and  $H_2O/CH_4 = 1$ ) and (c) steam reforming of upgraded biogas ( $H_2O/CH_4 = 1$ ).

$CO_2$  in the biogas feed increases, the  $H_2$  product reduces because the dry reforming of methane is more pronounced, inhibiting the decomposition of  $CH_4$ . Due to the endothermic dry reforming reaction, the demand of energy consumption to produce  $H_2$  increases when the reformer is operated at higher temperatures. An increase in the fraction of  $CO_2$  in the biogas feed promotes the dry reforming reaction and requires high energy for the reformer operation.

### 3.2 Steam reforming of biogas

Figure 3(b) shows the equilibrium composition of the synthesis gas product when biogas ( $CO_2/CH_4 = 0.5$ ) is fed to the steam reformer at the steam-to-methane ratio ( $H_2O/CH_4$ ) of one. The  $H_2$  fraction rapidly increases with increasing reforming temperatures, whereas the amount of  $CO_2$ ,  $CH_4$ ,  $H_2O$  and carbon is decreased. This is caused by the increase of the dry and steam reforming reactions and the reverse water gas shift reaction. At the operating temperature of  $800\text{ }^\circ\text{C}$ ,  $CH_4$  can completely react and the maximum concentration of  $H_2$  is obtained. The increased  $H_2O/CH_4$  ratio of the biogas feed increases the  $H_2$  yield because of the increased water gas shift reaction. Considering the heat requirement of the steam reformer, the increased reforming temperatures increase an external energy to supply to the steam reformer because the dry and steam reforming reactions of methane favor at high temperatures.

### 3.3 Steam reforming of upgraded biogas

The results from the previous section indicate that the steam reforming of biogas can generate hydrogen higher than the dry reforming process; however, the hydrogen product is diluted by the remaining  $CO_2$  in the biogas feed. A purification of biogas by removing  $CO_2$  would be attractive method to overcome this limitation. It is found that when biogas is sent to the MEA absorption process, 70 % of  $CO_2$  in the biogas feed is removed. However, this process needs more energy consumption up to about 939 kW. Regarding the steam reforming of the upgraded biogas, the mole fractions of  $H_2$  and  $CO$  in the obtained synthesis gas increase with increased reforming temperatures (Figure 3(c)). This result is caused from the endothermic steam reforming reaction and reverse  $CO$  reduction reaction. However, the fractions of  $CH_4$ ,  $H_2O$ , and  $CO_2$  shows an opposite trend because the steam reforming, reverse water gas shift, reverse  $CO$  disproportionation and reverse  $CO$  reduction reactions are more promoted. It is found that less external heat is required for the steam reformer when it is run at low temperatures as the amount of hydrogen is less produced.

Table 3 summarizes the optimum operating conditions of the different biogas reforming systems. The steam reforming of biogas is an appropriate method for hydrogen production from biogas because it provides the lowest energy consumption and no carbon formation. Under the optimal operating conditions, the maximum hydrogen yield of 2.66 is obtained at the reformer temperature of  $800\text{ }^\circ\text{C}$  with the feed ratio of  $CO_2/CH_4$  of 0.4 and  $H_2O/CH_4$  of one.

Table 3: Optimal conditions of the different reforming processes of biogas

Operating variable	DR-Biogas	SR-Biogas	SR-Upgraded biogas
CO <sub>2</sub> /CH <sub>4</sub> ratio	0.8	0.4	-
H <sub>2</sub> O/CH <sub>4</sub> ratio	-	1	1
Reaction temperature (°C)	1000	800	800
H <sub>2</sub> yield	1.99	2.66	2.86
Carbon formation (mole)	0.12	-	-
Heat duty (kW/kmole H <sub>2</sub> )	45.39	37.91	44.39
Hydrogen efficiency (%)	57.48	77.60	83.38

### 3.4 Integrated biogas processing and PEMFC system

In this part, the steam reforming process of biogas operated at its optimum conditions is investigated with the hydrogen purification process and PEMFC system. The conventional purification process consisting of water gas shift and preferential reactors, and the water gas shift membrane reactor are considered. At all studied cases, it is observed that the CO concentration is lower than the acceptable level for PEMFC operation (10 ppm). The simulation results also show that the current density of PEMFC increases with increased fuel utilization due to the higher amount of hydrogen consumed on the cathode side. Use of the water gas shift membrane reactor in the PEMFC system increases the current density, compared with that of the conventional water gas shift reactor, because more pure hydrogen is obtained. In addition, it is showed that the cell efficiency decreases with increased fuel utilization because high obtained current density decreases the cell voltage. When the PEMFC is operated at high temperatures, the cell voltage increases and more hydrogen is consumed, increasing the cell efficiency.

## 4. Conclusions

In this study, the integrated biogas processor and PEMFC system is studied based on a thermodynamic analysis. The performance of different biogas processing, i.e., dry reforming, steam reforming and steam reforming of upgraded biogas is investigated with respect to key operating parameters. It is found that the steam reforming of biogas is a suitable process for hydrogen production with minimization of energy demand and avoidance of carbon formation. Further, the performance of the biogas steam reforming process integrated with PEMFC is analyzed. The simulation results show that an increase in the fuel utilization has a negative effect on the fuel cell efficiency but high temperature operation of the PEMFC improves the fuel cell efficiency.

## 5. Acknowledgements

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