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Study on a Proton Exchange Membrane Fuel Cell System Fuelled by a Mixture of Bio-Ethanol and Methane

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Bio-ethanol is considered a good candidate for hydrogen production because of its renewability, low toxicity and high hydrogen content. In this work, the reforming process of a mixture of bio-ethanol and methane integrated with a proton exchange membrane fuel cell (PEMFC) is theoretically investigated. The simulation studies are performed using Aspen Plus simulator. The effect of operating parameters, such as temperature and feed ratio, on the concentrations of hydrogen and CO in the reformate gas is studied. The hydrogen fraction increases with increasing reformer temperatures until reaching its optimal point. An increase in the bio-ethanol to methane ratio ratio has a positive effect on the hydrogen production when the reformer is operated at the ratios lower than 1.25. The optimal conditions for reformer operation are the temperature of 900 °C and the bio-ethanol to methane ratio of 1. In addition, the reformer and PEMFC integrated system is studied and the result shows that the system efficiency of 35.2 % can be achieved.

1. Introduction

Traditionally, the conventional combustion-based process of petroleum-derived fuels is applied to power generation. However, this process has low efficiency and releases green house gas that is a major cause of global warming. Due to the need for clean energy and efficient technology, great efforts have been focused on development of fuel cells for electricity generation. Fuel cells can directly convert fuels to electricity through an electrochemical process and produces only water and heat as by-products when hydrogen is used as a fuel. Due to its high power density and rapid response to changes in power demand, the proton exchange membrane fuel cell (PEMFC) is a promising type of fuel cell for automotive, residential and portable applications.

In general, the reforming processes of fuels for hydrogen production can be classified into three common methods, namely, steam reforming (SR), partial oxidation (POX) and autothermal reforming (ATR) that combines the steam reforming and partial oxidation. Compared to the other processes, the steam reforming provides the highest hydrogen yield. It is also suitable for long periods of steady-state operation as in the stationary applications. To date, many non-renewable resources derived from fossil fuels have been utilized to produce hydrogen for fuel cells. Natural gas is among the most common resources used for hydrogen production in chemical industries for production of ammonia and alcohol (Farrauto, 2005). It generally consists of methane, as the major component, nitrogen, CO_2, ethane, propane, butane, pentane and some traces of other components (Patcharavorachot et al., 2013). Due to high H/C of methane, the reforming process of natural gas provides high hydrogen concentration. Heinzel et al. (2002) reported that the steam reforming of methane yields the highest hydrogen content of 75-78 vol.%. When fuel cells are

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fed by more pure hydrogen, their efficiency will be enhanced. For stationary applications, natural gas and LPG are good candidates for use in the hydrogen production process for PEMFCs (Adachi et al., 2009).

Regarding the environmental and availability aspects, renewable energy sources, such as, biomass, biogas and bio-ethanol, will become the most important feedstock for the production of hydrogen (Authayanun et al., 2013). These fuels are derived from agricultural products and plants, which consume CO_2 in their life cycles and offer a nearly closed carbon cycle. Liquid biofuels, especially bio-ethanol, have received significantly more attention than other fuels over the past few years as alternative fuel sources for PEMFC. Bio-ethanol is considered a good candidate for hydrogen production because of its renewability, low toxicity and high hydrogen content. It can be produced from several biomass sources, including energy plants, waste materials from agro-industrial wastes and forestry residue materials through fermentation process. However, the concentration of bio-ethanol obtained from the fermentation process is quite low about 8–12 wt.% (Iulianelli et al., 2010). To purify bio-ethanol, special distillation processes are necessary with high energy consumption. In general, the purified ethanol can be used in internal combustion engine (ICE); however, this method shows much lower efficient than its use for hydrogen production (Seelam et al., 2012).

In fact, bio-ethanol can be used as raw material for hydrogen production directly without requirement of purification steps because water in the bio-ethanol solution is a reforming agent. The excess water in ethanol drives the equilibrium-limited steam reforming reaction to the hydrogen product side; however, it dilutes the hydrogen product and the water removal step is required. Due to the water dilution effect in the bio-ethanol reforming process, the use of excess water to further produce hydrogen with other fuels is an interesting option. In this study, the steam reforming of a mixture of bio-ethanol and methane is considered, taking advantage of the excess of water present in the dilute bio-ethanol. The integration of the steam reforming process and PEMFC is theoretically investigated. The simulation studies are performed using Aspen Plus simulator. The effect of operating parameters, such as, temperature and feed ratio, on the fractions of hydrogen and CO in the reformate gas as well as the system efficiency is studied to find their optimal conditions.

2. PEMFC system

Typically, the integrated PEMFC system is demonstrated in Figure 1. The processing of fuels for PEMFC consists of reformer, water gas shift (WGS) and preferential oxidation (PROX) as the CO removal unit.

2.1 Fuel processor

The equilibrium composition of a reformate gas obtained from the methane and ethanol steam reforming is calculated from the direct minimization of Gibbs free energy. The total Gibbs free energy of a close reactive system at constant temperature and pressure decreases during the reaction proceeding and the equilibrium condition is reached when the total Gibbs free energy attains its minimum value.

$$\min_{n_i} (G^t)_{T,P} = \sum_{i=1}^{C} n_i \overline{G}_i = \sum_{i=1}^{C} n_i \left(G_i^\circ + RT \ln \frac{\overline{f}_i}{f_i^\circ} \right) \tag{1}$$

where C is the total number of components in the reaction system, n_i is the amount of mole of each gaseous component. Regarding the conservation of atomic species, n_i have to satisfy the element balance in Eq(2).

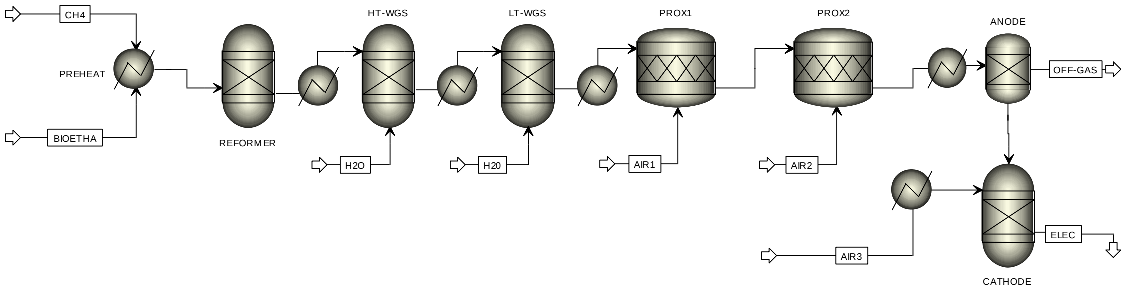

Figure 1: The steam reforming and PEMFC integrated system using a mixture of bio-ethanol and methane as fuel

Table 1: Models of voltage losses used in the PEMFC model (Authayanun et al., 2013)

Voltage loss	**Model**
Anode activation loss	$\eta_{\text{act,a}} = \frac{RT}{\alpha F}\sinh^{-1}\left(\frac{i}{2k_{\text{eh}}\theta_{\text{H}}}\right)$
Cathode activation loss	$\eta_{\text{act,c}} = \frac{RT}{\alpha F}\sinh^{-1}\left(\frac{i}{2i_0}\right)$
Ohmic loss	$K_{mem} = (0.5139\lambda - 0.326)\exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right)\right]\times 100$ $\eta_{\text{ohmic}} = \left(\frac{K_{\text{mem}}}{l_{\text{m}}}\right)i$

$$\sum_i n_i a_{ik} - A_k = 0 \qquad (k = 1, 2, ..., w) \tag{2}$$

where a_{ik} is the number of atoms of element k in component i, A_k is the total number of atoms of element k in the reaction mixture, and w is the total number of elements. The optimization problem mentioned above is to find the set of n_i which minimizes G_t for the specified T and P and satisfies the material balances.

The minimization of Gibbs free energy method is solved by representing reformer with the *Rgibbs* reactor module in Aspen plus simulator. The equation of state used in the calculation was based on the Peng-Robinson (PENG-ROB) method. The gaseous components appeared in the system are C_2H_5OH, CH_4, H_2, CO, CO_2, O_2, N_2 and H_2O. The possible reaction which can occur in the mixture of bio-ethanol and methane reforming are shown in Eq(3)-(6).

Ethanol steam reforming: $$C_2H_5OH + H_2O \ll 2CO + 4H_2 \tag{3}$$

Methane steam reforming: $$CH_4 + H_2O \ll CO + 3H_2 \tag{4}$$

Dry reforming of methane: $$CH_4 + CO_2 \ll 2CO + 2H_2 \tag{5}$$

Water gas shift reaction: $$CO + H_2O \ll CO_2 + H_2 \tag{6}$$

However, the reformate gases obtained from reformer generally contain some of CO which strongly adsorb on the surface of Pt and this results in catalyst deactivation. Therefore, the hydrogen purification process consists of the high and low temperature water gas shift reactors (WGSR) as well as the two stage preferential oxidation reactors (PROX). The high and low temperature WGSR are modelled as *Rgibbs* reactors and CH_4 is treated as an inert. In addition a *Rstoic* reactor is applied for the preferential oxidation (PROX) reactor**.**

2.2 PEMFC

For the PEMFC model, an ideal separator, *Sep* is applied for the anode to separate hydrogen from the reformate gas and the cathode is modeled as a *Rgibbs* reactor. The electrochemical reaction between hydrogen and oxygen in air occurs in this reactor. The basic relation of voltage and current density for PEMFC is described in Eq(7). The cell voltage (V_{cell}) can be calculated by subtracting the reversible cell potential (E_r), the maximum voltage that can be achieved by a fuel cell at specific operating condition, by the activation loss at the anode ($\eta_{\text{act,a}}$), the activation loss at the cathode ($\eta_{\text{act,c}}$) and the ohmic loss (η_{ohmic}). The detail of voltage loss model used in this study can be found in Table 1.

$$V_{\text{cell}} = E_r - \eta_{\text{act,a}} - \eta_{\text{act,c}} - \eta_{\text{ohmic}} \tag{7}$$

3. Results and discussion

The performance of a steam reforming of bio-ethanol for hydrogen production is thermodynamically analyzed under atmospheric pressure. A mixture of bio-ethanol and methane at different bio-ethanol to methane ratios and reformer temperature is investigated. In this work, the studied bio-ethanol consists of

10 % ethanol and 90 % water. Figure 2(a) shows the effect of operating temperature on the product composition. The temperature has a significant effect on the endothermic steam reforming reaction. At equilibrium condition, ethanol is completely reformed in all the temperature ranges considered. It is found that increasing the reforming temperature increases the molar flow of H_2 and CO but decreases CH_4 and CO_2. The effect of the bio-ethanol to methane ratios on the production of hydrogen is also shown in Figure 2(b). It is should be noted that the steam and ethanol feed stream in the reactive system increases with increasing the bio-ethanol to methane ratio. Therefore, an increase in bio-ethanol to methane ratio can shift the chemical equilibrium toward the product side and causes an increase in the molar flow of hydrogen produced. On the other hand, the change in CO shows an increase trend when bio-ethanol to methane ratio is increased until 1.2 but the CO content has slightly change at bio-ethanol to methane ratio > 1.2. In addition, hydrogen fraction at different reformer temperatures and bio-ethanol to methane ratios is shown in Figure 3(a). It is observed that the hydrogen fraction increase with reformer temperature until reaching the maximum point and then it does not change with this operating parameter. The increasing bio-ethanol to methane ratios have a positive effect on the hydrogen production when reformer is operated at bio-ethanol to methane ratios < 1.25. At higher than that point, the increasing bio-ethanol to methane ratios cause the reduction of hydrogen because of the dilution effect. The observed optimal reformer temperature and bio-ethanol to methane ratios from simulation results are 900 °C and 1.

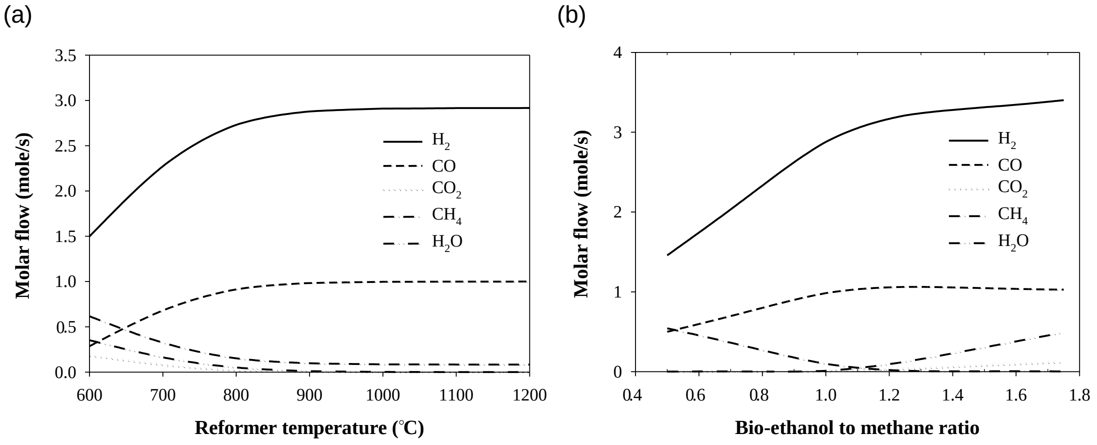

Figure 2: Molar flow of product gas at different operating conditions: (a) reformer temperatures and (b) bio-ethanol to methane ratios

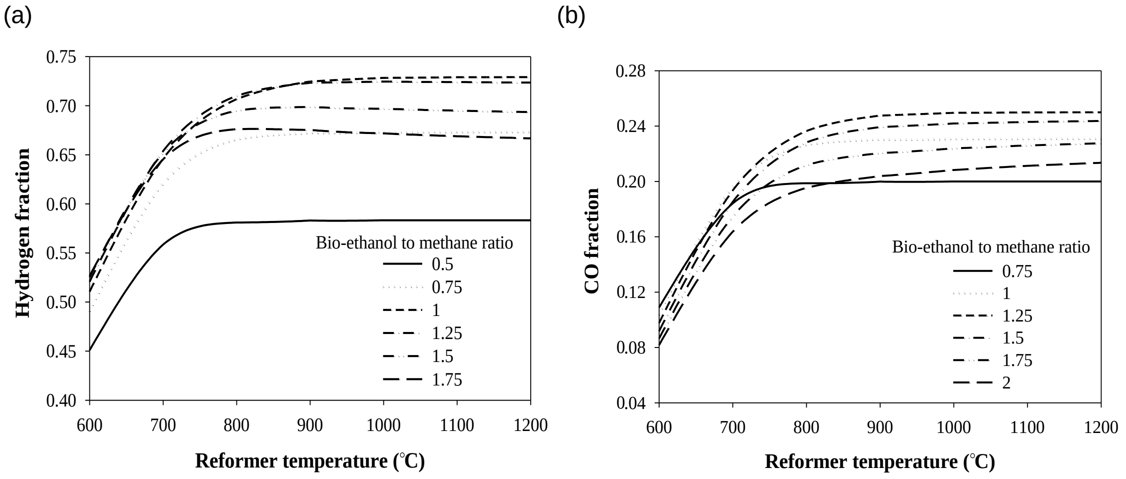

Figure 3: (a) Hydrogen fraction and (b) CO fraction at different reformer temperatures and bio-ethanol to methane ratios

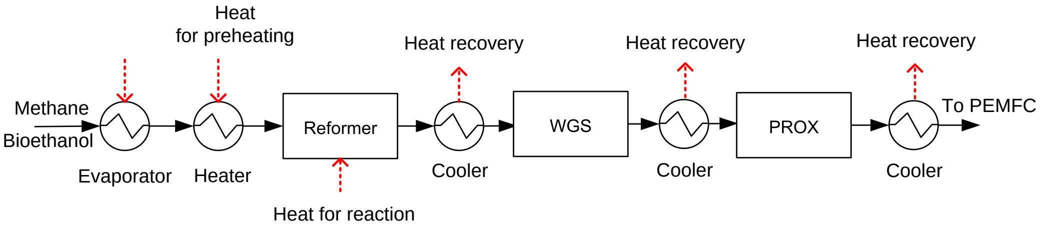

Figure 4: Heat management in the reforming and CO purification system

Table 2: The fractions of hydrogen and CO in the fuel processing process at optimal reformer operating condition

Units	Hydrogen fraction	CO fraction
Reformer	0.6536	0.1894
WGSR	0.6552	2.67×10^{-3}
First PROX	0.6401	1.32×10^{-4}
Second PROX	0.6394	< 10 ppm

Table 3: System Efficiencies

Parameters	Value
Total energy consumption (kW)	351.2
Fuel processing efficiency (%)	84.9
Fuel cell efficiency (%)	41.5
System efficiency (%)	35.2

Because the CO poisoning is a critical problem for PEMFC, the CO fraction at different reformer temperatures and bio-ethanol to methane ratios is studied and shown in Figure 3(b). From simulation results, it is found that CO fraction enhance when the reformer temperature increases up to 900 °C and it is unvarying at higher that value. The highest and lowest CO fraction is obtained at bio-ethanol to methane ratios of 1 and 0.75, respectively. Because the CO fraction is over limit of PEMFC and thus the CO purification process is also investigated. The high and low temperature WGS and PROX are used as CO removal units. At the optimal reformer operating condition (reformer temperature of 900 °C and bio-ethanol to methane ratio of 1), the observed hydrogen fraction and reduced CO fraction in each unit are shown in Table 2. The hydrogen fraction increase at WGSR and then reduces at two stages of PROX. This is because hydrogen is consumed via hydrogen oxidation reaction. However, the CO fraction is reduced to 0.01% at the first stage PROX which is over the limit of PEMFC and thus the second stage PROX is applied. At that reactor CO concentration is lower than 10 ppm. In addition, the heat requirement of reforming and CO purification process is also studied and represented in Figure 4. The heat requirement for the system is heat for preheating ($E_{preheating}$) including heat of vaporization, heat to maintain reformer ($E_{reforming}$) whereas recovery heat ($E_{recovery}$)is from hot reformate gas before being fed to high and low temperature WGSR and PROX. The heat release from hot gas is considered the recovered heat that can be used to preheat or vaporize reactant in the system. The total energy (E_{total}) used is calculated from Eq(8).

$$E_{total} = E_{preheating} + E_{reforming} - E_{recovery} \qquad (8)$$

The total energy consumption, fuel processing efficiency, fuel cell efficiency and system efficiency at optimal reformer operating condition are shown in Table 3. The main energy consumption in the system is from reformer unit and preheating unit. In addition, fuel cell efficiency and system efficiency are 41.5 % and 35.2 %, respectively when the value of operating cell voltage is 0.65. The using of bio-ethanol and methane mixture as fuel for hydrogen production has advantage over the using of purified bio-ethanol in term of the energy consumption because the distillation column requires a lot of energy for its operation.

4. Conclusions

Due to the renewability and dilution effect of bio-ethanol, the addition of methane into the steam reforming process of bio-ethanol to further use of excess steam is studied in this study. The reformate gas obtained from the reforming of a mixture of bio-ethanol and methane is used as a fuel for PEMFC system to produce electricity. The effect of reformer temperatures and bio-ethanol to methane ratio on the hydrogen production is revealed. From the simulation results, an increase in the reformer temperature and bio-ethanol to methane ratio shows the positive effect on the production of hydrogen. The observed optimal reformer temperature and bio-ethanol to methane ratios are 900 °C and one. The increasing bio-ethanol to methane ratio over its optimal value causes the reduction of hydrogen concentration because of the dilution effect. It is also observed that an increase in the bio-ethanol to methane ratio from 0.5 to 1 cause the increment of CO fraction in the reformate gas. From the PEMFC system analysis, the reformer and preheating units are the main sources of energy consumption in the system. When the steam reformer is operated under its optimal condition, the PEMFC system provides the efficiency of 35.2 %.

Acknowledgements

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