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Enhancement of Hydrogen Production for Steam Reforming of Biogas in Fluidized Bed Membrane Reactor

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Biogas is a promising source for hydrogen production to be supplied for fuel cell; however, biogas steam reforming process is operated at high temperatures and the obtained hydrogen-rich gas requires to be purified to improve the fuel cell efficiency due to its high component of carbon dioxide. A fluidized bed membrane reactor (FBMR), combining the reaction and the separation processes in single unit, is interesting option for hydrogen production from biogas. Therefore, the aim of this research is to analyze the hydrogen production from biogas via the steam reforming reaction in the FBMR. Firstly, a mathematical model based on the thermodynamic principal coupled with the hydrogen permeate rate via the membrane is developed to simulate a steam reforming process of biogas in the FBMR. To understand such a proposed reforming process, the comparison of biogas steam reforming in the conventional reformer (CR) and the FBMR is studied. The influence of key operating parameters of both the systems, such as temperature, reactor pressure as well as steam to carbon ratio, on the reactor performance in terms of the hydrogen production and purity is investigated. The result shows that the hydrogen product of biogas steam reforming in the FBMR is higher than that in the CR. The increase in the steam to carbon ratio has a minor influence on the hydrogen product in the FBMR while the hydrogen product of the FBMR rises considerably with increasing the operating temperatures and reactor pressure.

1. Introduction

The fuel cell and hydrogen production technologies have been developed rapidly in the last decade. In general, fuel cells need pure hydrogen as a fuel to produce the electricity. However, the production of hydrogen at acceptable cost and quality coupled with concern on the environmental problem is challenging. Biogas is considered an attractive and alternative raw material instead of fossil fuel for the hydrogen production because it is a cost effective and renewable fuel which can be produced bio-wastes such as municipal sewage, forestry residues, animal waste and organic matter through the anaerobic bacterial digestion. Use of biogas can also reduce the emission of CO_2 (Authayanun et al., 2013). A wide variety of processes is available for hydrogen production from hydrocarbon fuels, e.g. the steam reforming, partial oxidation, autothermal reforming and dry reforming. Piroonlerkgul et al. (2008) studied the performance of solid oxide fuel cell (SOFC) combined with the hydrogen production from biogas via the different reforming processes. The results showed that the steam reforming of biogas is the most suitable process combining with SOFC owing to its highest the power density. Although the steam reforming of biogas is suitable for hydrogen production for fuel cell, it needs to be operated at high temperatures caused by the thermodynamics equilibrium limitation. Saebea et al. (2013) reported that the biogas-fueled SOFC system requires the most energy and give the lowest power density compared with systems run on

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different fuels (i.e., methane and ethanol), due to the fact that biogas is composed of high CO_2 component that should be separated from the synthesis gas before utilizing for fuel cell.

To date, hydrogen is mostly produced via the steam reforming of light hydrocarbon in parallel fixed bed reactor. The fixed bed steam reformer suffers from a poor heat and mass transfers resulting in large temperature gradient and catalyst deactivation (Ammi et al., 2007). The reactor design is a crucial main issue for the improvement of hydrogen production. A fluidized bed reactor has been proposed to replace the fixed bed steam reformer. The advantages of fluidized bed reactor include a good heat and mass transfer capability, leading to more uniformity of temperature distribution, an elimination of catalyst diffusion limitation as well as more compact design (Rahimpour et al., 2009). Furthermore, to overcome the thermodynamics equilibrium restriction, the membrane technology is applied to the fluidized bed reactor called “fluidized bed membrane reactor (FBMR)”. The FBMR integrates the reaction and separation processes in a single unit. More recent research has studied the FBMR for the methane steam reforming. Due to the complication of the FBMR, various models of the FBMR for methane steam reforming have also been proposed to study the effect of operational variables on the performance of FBMR (Ye et al., 2009) similar results presented Mahecha-Botero et al.,(2009) and later Bayat and Rahimpour (2013). However, there are few theoretical and experimental studies on the production of hydrogen from the biogas steam reforming in FBMR. In this study, the FBMR is investigated to improve the hydrogen production from the steam reforming of biogas. The thermodynamic model of the FBMR coupled with the permeation rate of membrane is developed and employed to analyze its performance in term of the hydrogen production with respect to key operating conditions, such as temperatures, steam to carbon, reactor pressure, and biogas composition on the hydrogen production. To indicate the suitability of the FBMR for biogas steam reforming, performance of the FBMR is compared with the equilibrium reactor, which is called the conventional reformer (CR) in this work.

2. Model of fluidized bed membrane reactor (FBMR)

Figure 1 illustrates the FBMR for the biogas steam reforming. Biogas is mixed with the steam before it is fed to the reactor while sweep gas is introduced to permeate side of the membrane. The steam reforming reactions of biogas taking place in the FBMR are shown in Eq(1)-(3). The reformed gas (i.e., H_2, CO, CO_2, H_2O and CH_4) is produced and hydrogen is selectively permeated through the membrane. Hydrogen is retrieved from the reactor zone with sweep gas. The model describing the FBMR is developed based on the following assumptions; the system is operated under the steady state condition and reaches thermodynamic equilibrium, all gaseous components behave as ideal gases, the reactor temperature is uniform owing to the rapid and perfect mixing of the solid and reacting gas, heat and pressure losses are negligible, and only hydrogen can penetrate through the membrane.

2.1 Biogas steam reforming

Main reactions of the biogas steam reforming are as shown below:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_{298} = +206.2 \text{ kJ/mol} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_{298} = -41 \text{ kJ/mol} \tag{2}$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H_{298} = +247.9 \text{ kJ/mol} \tag{3}$$

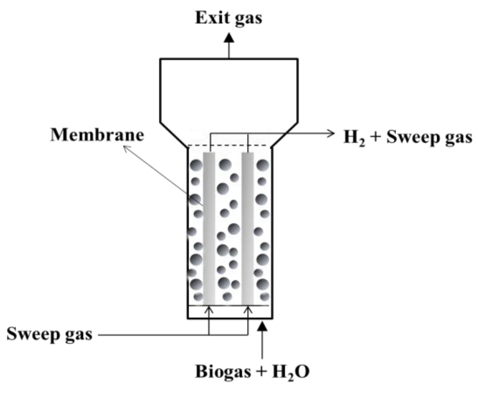

Figure 1: Schematic diagram of a fluidized bed membrane reactor

Thermodynamically analysis of the biogas reforming system is based on a stoichiometric approach. The molar flow rates of each component in the reformate gas are given by the following expressions:

$$n_{CH_4} = a_{CH_4} - x_1 \tag{4}$$

$$n_{CO_2} = a_{CO_2} + x_2 \tag{5}$$

$$n_{H_2O} = b - x_1 - x_2 \tag{6}$$

$$n_{H_2} = 3x_1 + x_2 \tag{7}$$

$$n_{CO} = x_1 - x_2 \tag{8}$$

$$n_{total} = a_{\mathrm{CH_4}} + a_{\mathrm{CO_2}} + b - 2x_1 + 2x_2 \tag{9}$$

where a_{CH4}, a_{CO2} and b represent the inlet molar flow rate of methane, carbon dioxide and water, x_1 and x_2 are the extent of reactions Eq(1) and (2). The equilibrium constants of all the reactions can be determined form the Van't Hoff equation as given by Eq(10). As all the reactions take place in the gas phase, the equilibrium constant can be expressed in terms of pressure and composition as follows:

$$\frac{d \ln K}{dT} = \frac{\Delta H^{\circ}}{RT^2} \tag{10}$$

$$\prod_i (y_i \phi_i)^{v_i} = \left(\frac{P}{P^0}\right)^{-v} K \tag{11}$$

$$v = \sum_i v_i \quad \text{and} \quad y_i = \frac{n_i}{\sum_i n_i} \tag{12}$$

where K, T, P, P^0, R and ΔH^0 represent the equilibrium constant, the temperature, the total pressure, the standard pressure, the gas constant and the heat of reaction, respectively, y_i, v_i and ϕ_i are, the mole fraction, the stoichiometric coefficient and the fugacity coefficient of the component i.

2.2 Separation model

Generally, Pd or Pd-Ag membrane is utilized for the hydrogen-selective membrane; however, Pd-Ag membrane is preferable due to its high hydrogen-selective membrane. The hydrogen permeation through the Pd-Ag membrane (Xie et al., 2013) can be explained by Sievert's Law as follows:

$$J_{\mathrm{H_2}} = \eta k C_{ep} [p_{\mathrm{H_2,r}}^{1/2} - p_{H_2,p}^{1/2}] \tag{13}$$

$$k = k_0 \exp\left(-\frac{Ea}{RT}\right) \tag{14}$$

where $p_{H2,p}$ and $p_{H2,r}$ are the hydrogen partial pressures in the permeate side of the membrane and the reactor side, η is the permeation effectiveness factor, C_{ep} is the permeation capacity depended on the membrane surface area and thickness, k is the pre-exponential factor and Ea is the activation energy for permeation.

3. Simulation approach

In this work, the biogas steam reforming in the FBMR is compared with the conventional reformer (CR). The conventional reformer of biogas steam reforming can be simulated from the steam reforming reaction of biogas model at the equilibrium condition described in the Section 2.1. For the FBMR, the model is divided to two parts which are the sub-reformer of biogas steam reforming process and the sub-separator with membrane. The model equations explaining the biogas steam reforming process and hydrogen separation through the membrane in Section 2.1 and 2.2 are solved by using MATLAB solver. The FBMR model has numerous reformer and separator submodels. Firstly, the number of reformer submodels (m) is guessed. The value of m used for the simulation of FBMR model should be determined without affecting the amount of hydrogen flux through the membrane when the value of m is increased. To ensure the reliability of the FBMR model, it was verified with the result data of Ye et al. (2008). The molar flow rate of products and the permeation of hydrogen rate predicted from the simulation show good agreement with the published data.

4. Results and discussion

The nominal conditions for the simulation study on of the biogas steam reforming in the FBMR and CR to produce hydrogen is summarized in Table 1. Figure 2a shows the influence of the operating temperatures on the hydrogen product of biogas steam reforming in the CR and in the FBMR when biogas with different compositions is used. Comparing to the CR, the FBMR provides more hydrogen product in the FBMR because the hydrogen-selective membrane, installed in the FBMR to separate hydrogen from the reaction zone, assists to drive the steam reforming reaction forwardly. When considering the composition of biogas, the main reactant in the biogas converted to hydrogen is methane while the carbon dioxide might be reactant for reacting with methane to produce hydrogen in the dry reforming. However, the dry reforming is less pronounce when the excess steam in the reforming process and the carbon dioxide as the product of biogas steam reforming reactions added to the system has an impact on the occurrence of reverse reaction. Thus, the increment of carbon dioxide content in the biogas results in reducing the hydrogen product in both systems.
In both systems, the hydrogen product is raising with increasing the operating temperature due to the steam reforming reaction as the endothermic reaction. The increment of the hydrogen product of the biogas steam reforming in the FMBR. The increase of the operating temperature for the biogas steam reforming reactions in the FBMR has more the positive influence on increment of the hydrogen product than the CR at the temperature range of 673 to 923 K. In the FBMR, the capacity of membrane permeability is also improved with an increase in operating temperature as shown in Figure 2b. The hydrogen product is retrieved further from the reaction zone when increasing the operating temperature. Nevertheless, the capacity of hydrogen-selective membrane in the present is limited at the operating temperature of 923 K.

Table 1: Nominal condition for the study of key operating parameters

Parameter	Value	Parameter	Value
Operating temperature (K)	873	permeation effectiveness factor (-)	1
Reactor pressure (MPa)	2	Permeation capacity (km)	40
Steam to carbon ratio (-)	3	Activation energy for permeation (kJ mol^{-1})	$9.18x10^{3}$
Inlet flow rate of biogas (kmol h^{-1})	1	Pre-exponential factor (mol $km^{-1}Pa^{-0.5}s^{-1}$)	$6.55x10^{-3}$
Permeate pressure (MPa)	0.1	Sweep gas flow (kmol h^{-1})	10

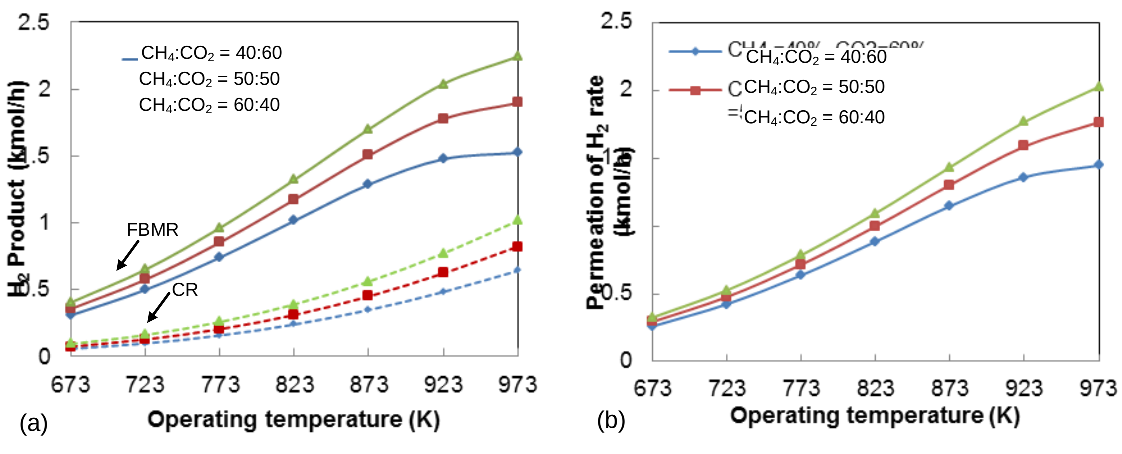

Figure 2: Effect of operating temperature at varied composition of biogas on (a) the hydrogen product of the biogas steam reforming reactions compared between the CR (dash line) and the FBMR (thick line) (b) the permeation of hydrogen rate

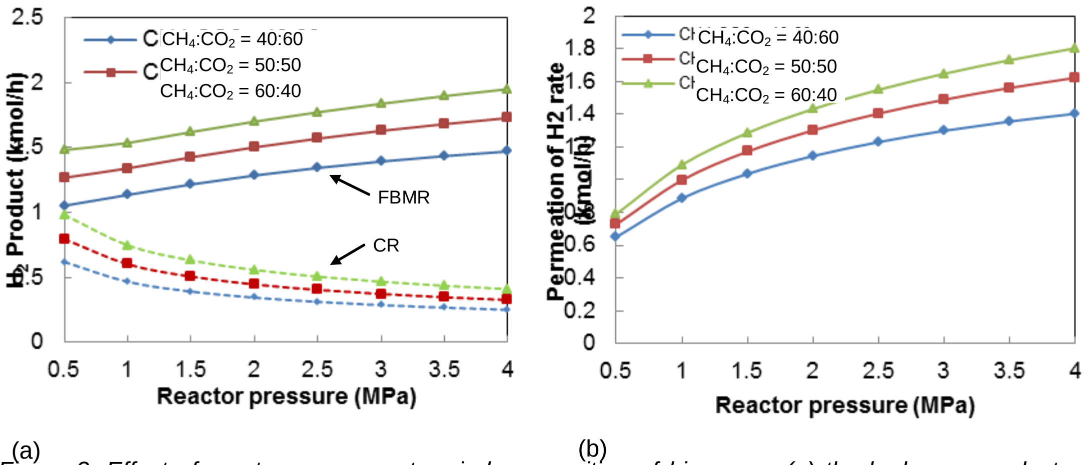

Figure 3: Effect of reactor pressure at varied composition of biogas on (a) the hydrogen product of the biogas steam reforming reactions compared between the CR (dash line) and the FBMR (thick line) (b) the permeation of hydrogen rate

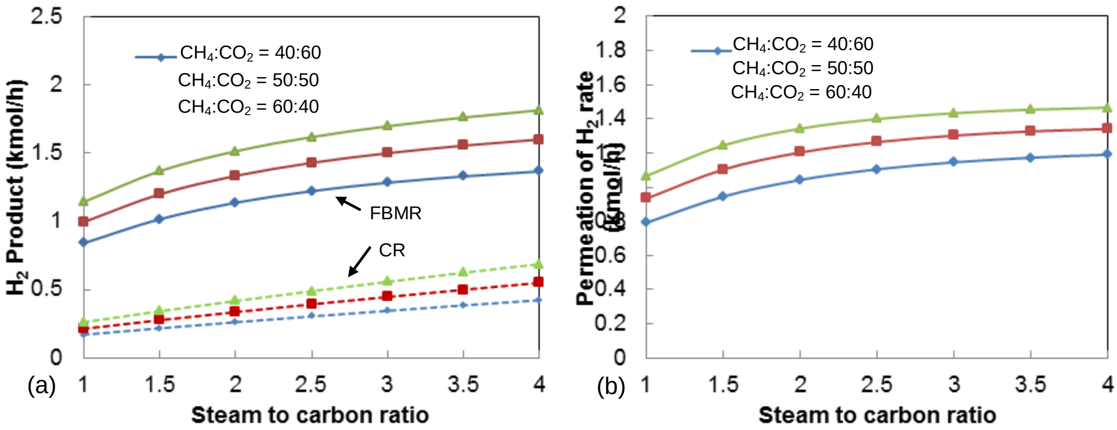

Figure 4: Effect of steam to carbon ratio at varied composition of biogas on (a) the hydrogen product of the biogas steam reforming reactions compared between the CR (dash line) and the FBMR (thick line) (b) the permeation of hydrogen rate

The influence of reactor pressure on the hydrogen product of biogas steam reforming reactions in the CR and the FBMR is shown in Figure 3a. It can be seen that the increase of the reactor pressure on the hydrogen product of the biogas steam reforming in the CR has an inverse characteristic with that in the FBMR. The hydrogen product of biogas steam reforming in the CR decreases whereas the hydrogen product in the FBMR would be raised with the increase of operating pressure. According to LeChatelier's principle, the steam reforming reaction of biogas is favoured at low pressure; hence, the hydrogen product in the CR is reduced when the reformer is operated at higher pressure. At high pressure, the reactor pressure has an insignificant effect on the decrement of hydrogen product of biogas steam reforming in the CR. For the FBMR, the effect of a decrease of hydrogen product with an increase of reactor pressure becomes lower due to the removal of hydrogen product through the membrane from reaction zone. The higher reactor pressure aid to increasing of the driving force of hydrogen permeated through membrane from the reaction zone to the permeated side, leading to higher the hydrogen product separated from the system of reforming reaction. Consequently, the steam reforming reaction will shift towards the products further as seen in Figure 3b.

Figure 4a shows the effect of steam to carbon ratio on hydrogen product at varied composition of biogas. An addition of the steam within the steam reforming reaction of biogas can increase in driving a reaction in forward direction. In both systems, the hydrogen product would be improved if the steam to biogas ratio is increased. Nonetheless, the biogas steam reforming in the CR is a higher increment of hydrogen product than that in the FBMR. The excessive steam in the system of FBMR results in the concentration of hydrogen product diluted, leading to the decrease of hydrogen partial pressure. Consequently, the difference of hydrogen partial pressure between the reactor and permeate side diminishes and the push of hydrogen product to remove from reaction zone subsides. As seen in Figure 4b, the permeation of hydrogen rate is slightly elevated with increasing the inlet steam.

5. Conclusions

In this work, a thermodynamic analysis of the biogas steam reforming in a fluidized bed membrane reactor (FBMR) and conventional reformer for hydrogen production was performed. The FBMR model was developed, which was divided into two main submodels: the sub-reformer and the membrane sub-separator based on the Sievert's Law, whereas the CR model was based on the biogas steam reforming at an equilibrium condition. Effect of key operating factors on the performance of the FBMR was studied and the simulated results indicated that the FBMR achieves considerably high hydrogen product for the biogas steam reforming, compared with the CR. The increase of temperatures and pressure in a suitable operational range has a positive effect on hydrogen product and the hydrogen permeation rate in the FBMR system. However, the addition of high steam in the biogas feed reduces the hydrogen concentration.

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