Adsorption-membrane hybrid system for ethanol steam reforming: Thermodynamic analysis

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Abstract
In this study, an adsorption-membrane hybrid system in which a carbon dioxide adsorbent is used to remove undesired carbon dioxide and a membrane is applied for hydrogen separation is theoretically investigated with the aim to improve the performance of an ethanol steam reforming. A thermodynamic analysis of such the system was performed and compared with a membrane reactor and an adsorptive reactor. It was found that the removal of hydrogen by membrane separation has higher impact on the reformer performance than the carbon dioxide capture by adsorption. The adsorption-membrane hybrid system for ethanol steam reforming gives the highest hydrogen yield. Considering a possibility for carbon formation, the simulation results showed that the use of membrane for pure hydrogen production increases the trend toward carbon formation. This is due to an increase in carbon monoxide concentration in the reaction zone that promotes the Boudouard reaction. In contrast, the use of carbon dioxide adsorbent reduces the formation of carbon as carbon monoxide is less generated in the system.

1. Introduction

Hydrogen is a major fuel for electricity generation in fuel cells; however, its uses are still facing with several issues such as its economical production, storage and distribution [1]. In general, hydrogen can be derived from primary fuels such as natural gas, methanol, ethanol, gasoline, and coal via a fuel processor. Among all possible fuels, ethanol has been considered as an attractive green fuel since it can be produced renewably from the fermentation of various biomass sources, including energy plants, organic fraction of municipal solid waste, waste materials from agro-industries, or forestry residue materials [2]. Moreover, the use of ethanol for producing hydrogen offers some advantages as it is easy to store, handle, and transport in a safe way due to its lower toxicity and volatility [3,4].

Considering a fuel processor, there are three main reactions (i.e., steaming reforming, dry reforming, and partial oxidation) used to reform ethanol into hydrogen-rich gas; however, the ethanol steam reforming provides a higher hydrogen yield, compared to the other reforming processes [5]. Ethanol steam reforming has been widely investigated based on thermodynamic [2] and experimental studies [6,7]. Thermodynamic
studies indicated that at atmospheric pressure, the steam reforming of ethanol can achieve high hydrogen production at temperatures higher than 1000 K because it is limited by the thermodynamic equilibrium of the reversible reforming reaction. Furthermore, the operation of ethanol steam reforming consumes high energy and needs expensive alloy reformer tubes [8]. The problem on purifying hydrogen is another issue in hydrogen production. Consequently, a new concept for the production of hydrogen with lower operating and capital costs compared to a conventional reforming process is desired.

The use of membrane reactors for improving the ethanol steam reforming process is one of the interesting options to be considered due to the integration of two different processes (reaction and separation) in a single unit. For this purpose, hydrogen as a desired product is selectively removed through the membrane and thus, it is possible to overcome the thermodynamic limitation [9,10]. In addition, the increased reaction rate leads to a reduction in the operating temperature and consequently the energy requirement [11]. However, hydrogen produced from the membrane reactor still contains substantial amount of undesired by-products and a treatment unit is also needed to remove such the undesired by-products before its subsequent use in fuel cell powered vehicles [12].

An alternative way to enhance the hydrogen production is the addition of a carbon dioxide adsorbent in reforming reactors [13–17]. A hybrid system of adsorption and membrane processes in a single unit is considered as a very promising technique for hydrogen production via steam reforming reaction. Carbon dioxide adsorbent is used to remove undesired carbon dioxide, whereas hydrogen is separated from the reforming reaction by a hydrogen selective membrane. Therefore, the adsorption-membrane hybrid system shows good potential to obtain pure hydrogen without the requirement of shift reactors. This would result in a reduction in operating temperature, providing low operating and capital cost [16].

In this study, a thermodynamic analysis of ethanol steam reforming with and without the presence of carbon dioxide adsorbent and hydrogen selective membrane is presented. A comparison among a conventional reformer, membrane reactor, adsorptive reactor and adsorption-membrane hybrid system is performed to determine the suitable process of ethanol steam reforming. The effect of operating conditions, i.e., temperature, steam to ethanol ratio, and fraction of carbon dioxide and/or hydrogen removal, on an equilibrium composition of the reforming products is investigated. In addition, the boundary of carbon formation in the ethanol steam reforming system is considered. It is noted that although the study on the adsorption-membrane hybrid system is performed based on a thermodynamic analysis, this would demonstrate the possibility of applying the adsorption-membrane hybrid system for hydrogen production from ethanol.

2. Theory

In this study, a thermodynamic analysis of ethanol reforming systems is performed by using a stoichiometric approach to compute the equilibrium composition of reformed products. In the ethanol steam reforming, the following reactions are considered [18].

\[
\begin{align*}
C_2H_5OH + H_2O & \rightarrow 4H_2 + 2CO \quad (1) \\
CO + H_2O & \rightarrow H_2 + CO_2 \quad (2) \\
CO + 3H_2 & \rightarrow CH_4 + H_2O \quad (3)
\end{align*}
\]

The equilibrium constants of all the reactions can be determined from the Van’t Hoff equation (Eq. (4)) as

\[
d\ln K = \frac{\Delta H^0}{R} \frac{1}{T}
\]

where \(K\), \(T\) and \(R\) represent, respectively, the equilibrium constant, the operating temperature and the gas constant, and \(\Delta H^0\) is the heat of reaction.

As all the reactions take place in the gas phase, the equilibrium constant can be expressed in terms of pressure and composition as follows:

\[
\Pi(y_i, \phi_i) = \left(\frac{P}{P_0}\right)^{n_i - \frac{1}{2}}
\]

\[
v = \sum_{i} v_i \text{ and } y_i = \frac{n_i}{\sum_j n_j}
\]

where \(P, P_0, y_i\) and \(v_i\) are the total pressure, the pressure at standard condition (1 bar), the mole fraction of the component \(i\), and the stoichiometric coefficient, respectively, and \(\phi_i\) is the fugacity coefficient of the component \(i\).

For the computation of equilibrium compositions, the gaseous mixture was assumed to be an ideal gas and thus the equilibrium constant of each reaction (Eqs. (1)–(3)) can be written as:

\[
K_1 = \frac{y_{CO}^2 y_{H_2}^4}{y_{C_2H_5OH} y_{H_2O}} P^4
\]

\[
K_2 = \frac{y_{CO} y_{H_2}}{y_{CO} y_{H_2O}}
\]

\[
K_3 = \frac{y_{CH_4} y_{H_2O}}{y_{CO} y_{H_2}} P^{-2}
\]

The molar flow rates of each component for the reactions in the ethanol steam reforming process are given by the following expressions:

\[
r_{C_2H_5OH} = a - x_1
\]

\[
r_{H_2O} = b - x_1 - x_2 + x_3
\]

\[
r_{H_2} = 4x_1 + x_2 - 3x_3
\]

\[
r_{CO} = 2x_1 + x_2 - x_3
\]

\[
r_{CH_4} = x_3
\]

\[
r_{CO_2} = x_2
\]

\[
n_{total} = \sum_{i=1}^{6} n_i = a + b + 4x_1 - 3x_2
\]

where \(a\) and \(b\) represent the inlet molar flow rate of ethanol and water and \(x_1, x_2\) and \(x_3\) are the extent of reactions (1)–(3), respectively.
In an adsorption-membrane hybrid system of ethanol steam reforming, carbon dioxide adsorbent is mixed with steam reforming catalyst in a membrane reactor; carbon dioxide is removed from the reaction zone by adsorbent whereas hydrogen is separated from the reaction zone by membrane. Considering the carbon dioxide adsorption and the hydrogen separation in the ethanol steam reforming process, the molar flow of carbon dioxide and hydrogen are expressed as:

\[ n_{CO_2} = x_2 - fx_2 \]  
\[ n_{H_2} = 4x_1 + x_2 - 3x_3 - r(4x_1 + x_2 - 3x_3) \]

where \( f \) is the fraction of carbon dioxide that is removed by adsorption and \( r \) is the fraction of hydrogen that is removed through membrane. As a result, the total moles of all species in the gas phase are decreased as shown below:

\[ n_{total} = \sum_{i=1}^{6} n_i = a + b + 4x_1 - 3x_2 - fx_2 - r(4x_1 + x_2 - 3x_3) \]

It is noted that for an adsorptive reactor, the composition of gases produced can be computed by setting the fraction of hydrogen removal through membrane to be zero. On the contrary, the fraction of carbon dioxide removal by adsorption equals to zero when a membrane reactor is applied to ethanol steam reforming.

The most possible reactions that can lead to the formation of carbon in the ethanol reforming system are as follows:

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C} \]  
\[ \text{CH}_4 \rightarrow 2\text{H}_2 + \text{C} \]  
\[ \text{CO} + 2\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{C} \]  
\[ \text{CO}_2 + 2\text{H}_2 \rightarrow \text{H}_2\text{O} + \text{C} \]

In this study, the thermodynamic analysis of the carbon formation is examined by considering the Boudouard reaction (Eq. (20)) since it shows the lowest value of Gibbs free energy. The possibility of carbon formation can be calculated from the value of carbon activity as defined:

\[ a_c = \frac{K_a x_{CO_2}^2}{x_{CO_2}} \]

where \( a_c \) is the activity coefficient of carbon and \( K_a \) represents the equilibrium constant of the Boudouard reaction.

In case of the carbon activity greater than unity, the system is not in equilibrium and the carbon formation is present. When the carbon activity equals to unity, the system is in equilibrium. Finally, at the carbon activity less than unity, the formation of carbon is thermodynamically impossible to occur in system. It is noted that the carbon activity is only an indicator for determining the presence of carbon in system and thus, an amount of carbon formation cannot be examined.

It is to note that in this study, the analysis of ethanol reforming systems is performed based on a theoretical study and thus, types of membrane and carbon dioxide adsorbents are not considered here. The set of the formulated nonlinear equations for computing the molar flows of each component at the equilibrium condition is solved by using MATLAB.

3. Results and discussion

3.1. Ethanol steam reforming without carbon dioxide adsorbent and hydrogen selective membrane

In this section, a thermodynamic analysis of ethanol steam reforming process without the removal of carbon dioxide by adsorption and hydrogen by membrane (referred to a conventional process) is presented. At the standard conditions, the inlet molar flow rate of ethanol is 1 mol/s and steam to ethanol ratio is 3. Since the reformer temperature is identified as a key parameter having a significant effect on the hydrogen production, the distribution of the reformed products at different operating temperatures is analyzed as shown in Fig. 1. The results indicate that the amount of hydrogen increases rapidly with increasing temperatures from 673 K to 973 K and reaches its maximum value at 1073 K, whereas the opposite trend is observed for methane. This is because the strong endothermic steam reforming reaction is favored at higher temperatures. Furthermore, an increase in operating temperature strongly raises carbon monoxide as water gas shift reaction (Eq. (2)) is less pronounced. As can be seen in Fig. 1, the content of carbon monoxide in the synthesis gas obtained is rather high. This would indicate that the synthesis gas product with high carbon monoxide content may not be suitable for direct use in low temperature fuel cell stack like PEMFC unless there is a carbon monoxide treatment unit.

Fig. 2 shows the effect of steam to ethanol ratio on the equilibrium compositions of ethanol steam reforming at \( T = 1073 \) K and \( P = 1 \) bar. When more steam is added in the system, the water gas shift reaction (Eq. (2)) can be driven forwardly and thus, hydrogen is more produced whereas carbon monoxide shows the opposite trend. However, the unreacted steam may lead to the dilution effect of hydrogen so that the choice of the steam to ethanol ratio should be carefully considered. The effect of operating pressure on the
ethanol steam reforming is shown in Fig. 3. The simulation results show that increasing operating pressure leads to a decrease in hydrogen, carbon dioxide and carbon monoxide. For this reason, operation of the ethanol steam reforming in the conventional steam reformer at the atmospheric pressure is considered to be a suitable condition.

From the above results, it is indicated that both the steam to ethanol ratio and the temperature have significant effects on the hydrogen production. Fig. 4 presents the influence of the steam to ethanol ratio at different operating temperatures on the hydrogen produced at atmosphere pressure. From Fig. 4, it can be seen that the optimal condition of the ethanol steam reforming in the conventional reformer is at the temperature of 1073 K and the steam to ethanol feed ratio of 5. Due to the equilibrium reactions, the maximum hydrogen produced is 4.9 mol/s. According to the reaction stoichiometry, for the steam reforming process, 1 mol of ethanol can provide 6 mol of hydrogen product. In order to improve the performance of hydrogen production, the removal of carbon dioxide by an adsorption process and the separation of hydrogen by a membrane should be considered.

3.2. Ethanol steam reforming with carbon dioxide adsorbent and/or hydrogen selective membrane

3.2.1. Effect of carbon dioxide removal
When carbon dioxide adsorbent is mixed with catalyst in an absorptive reactor, carbon dioxide, the undesired product produced in the ethanol steam reforming process, is removed by adsorption. Fig. 5 demonstrates the effect of carbon dioxide removal from the steam reforming system on the equilibrium compositions of the reformed products. Increasing the fraction of carbon dioxide removal slightly promotes the water gas shift reaction, improving hydrogen production and reducing carbon monoxide in the system. The use of carbon dioxide absorbent also decreases the content of carbon dioxide remaining in the reforming system.

3.2.2. Effect of hydrogen removal
The production of hydrogen from ethanol steam reforming is carried out in a membrane reactor. The effect of fraction of hydrogen removal on the performance of ethanol steam
reforming is investigated as demonstrated in Fig. 6. The results show that the content of hydrogen in the reformed product decreases with increasing the fraction of hydrogen removal. However, the total amount of hydrogen produced, sum of hydrogen in permeate and retentate streams, considerably increases. When hydrogen is increasingly removed from the system, the water gas shift and the reversed methanation reactions become more pronounced as observed from an increase in carbon dioxide and a decrease in methane.

Comparing with the case of carbon dioxide removal by the adsorption, it indicates that the selective separation of hydrogen via the membrane offers higher hydrogen production of the ethanol steam reforming. As the hydrogen is generated at higher content than the carbon dioxide, the removal of hydrogen has more effect on the ethanol reforming system. However, it is found that the amount of carbon monoxide becomes lower when the carbon dioxide absorbent is applied to the system. As a result, the fractions of hydrogen and carbon dioxide removal are key design parameters for the ethanol reforming process to obtain high purity of hydrogen with less carbon monoxide.

3.2.3. Simultaneous removal of carbon dioxide and hydrogen

In this section, a thermodynamic analysis of ethanol steam reforming in an adsorption-membrane hybrid system is performed. Fig. 7a–d show the effects of simultaneous removal of carbon dioxide and hydrogen on the equilibrium compositions of the reformed products, i.e., hydrogen, methane, carbon

![Fig. 6](image)

**Fig. 6** — Effect of fraction of hydrogen removal ethanol steam reforming ($T = 873\ K$, $P = 1\ \text{bar}$, and ethanol to steam ratio = 3).

![Fig. 7](image)

**Fig. 7** — Effect of the removal fraction of carbon dioxide and hydrogen in the adsorption-membrane hybrid system ($T = 873\ K$, $P = 1\ \text{bar}$, and ethanol to steam ratio = 3): (a) hydrogen, (b) methane, (c) carbon monoxide, and (d) remaining carbon dioxide.
monoxide, and remaining carbon dioxide, respectively. As hydrogen separation is carried out along with carbon dioxide capture, the reversible reforming reactions are more driven to the product side, compared to the use of either an adsorptive or a membrane reactor. Increasing the fractions of hydrogen and carbon dioxide removal highly increases the amount of hydrogen, whereas the methane content deceases (Fig. 7a–b). Fig. 7c shows that the capture of carbon dioxide in the ethanol reforming system has strong effect on the content of carbon monoxide, compared to the removal of hydrogen. Moreover, it can be seen that the increased fraction of carbon dioxide removal leads to a reduced carbon dioxide content remaining in the reforming system, whereas increasing the hydrogen removal fraction gives an increased trend as shown in Fig. 7d. Therefore, addition of carbon dioxide adsorbent in the membrane reactor results in further purifying hydrogen in the reaction zone due to a decrease in the amount of carbon dioxide and carbon monoxide.

3.3. Carbon formation in ethanol steam reforming systems

Generally, an excess steam is required for fuel reforming processes to promote water gas shift reaction, resulting in an increase in the amount of carbon dioxide. Higher carbon dioxide concentration can prevent the formation of carbon from the Boudouard reaction. Consequently, the boundary of possible carbon formation can be defined from the less requirement of steam fed to the reforming system. In this section, the impact of operating temperatures on the steam to ethanol ratio required to avoid carbon formation in the ethanol steam reforming systems is investigated at different fractions of carbon dioxide and hydrogen removal.

Fig. 8 shows the requirement of inlet steam to ethanol ratio as a function of operating temperatures for the adsorption-membrane hybrid system of ethanol steam reforming. The region on the left side under the boundary line is the area where carbon formation may occur. It is found that at the fixed fraction of carbon dioxide removal (f = 0.8), the possibility of carbon formation is more pronounced even the fraction of hydrogen removal is slightly increased (r = 0 → r = 0.2). On the other hand, the tendency of carbon formation in the adsorption-membrane hybrid system with a less removal of carbon dioxide (r = 0.8, f = 0.2) at a low temperature range (500–800 K) decreases when compared with the reforming system using only a membrane (r = 0.8, f = 0). As a result, it can be concluded that addition of carbon dioxide adsorbent in the membrane reactor alleviates the occurrence of carbon. Considering the amount of steam required for this system, increasing the fraction of carbon dioxide adsorption in the membrane reactor (r = 0.8, f = 0.8) results in a significant reduction in the requirement of steam fed to the system at low temperature of 500–800 K. However, when the operating temperature is higher than 850 K, the boundary of carbon formation of the adsorption-membrane hybrid system is greater than the use of the hydrogen selective membrane reactor.

4. Conclusions

This study presented the thermodynamic analysis of ethanol steam reforming in the adsorption-membrane hybrid system in which carbon dioxide adsorbent is used to remove undesired carbon dioxide and membrane is applied for hydrogen separation. Effects of operating conditions, i.e., temperature and steam to ethanol ratio, on hydrogen production were investigated. The results showed that at atmospheric pressure, the production of hydrogen from the ethanol steam reforming is favored at high steam to ethanol ratio and temperature. Considering the adsorption-membrane hybrid system, it was found that hydrogen removal by membrane separation has more impact on the reactor performance than carbon dioxide removal by adsorption. However, the boundary of carbon formation is likely to decrease when carbon dioxide adsorption is considered. The use of the adsorption-membrane hybrid system in ethanol steam reforming process does not only provide the highest hydrogen yield but also obtain pure hydrogen product.

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