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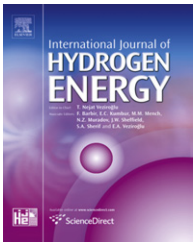

Adsorption-membrane hybrid system for ethanol steam reforming: Thermodynamic analysis

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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 ago-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

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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].

$$C_2H_5OH + H_2O \leftrightarrow 4H_2 + 2CO \tag{1}$$

$$CO + H_2O \leftrightarrow H_2 + CO_2 \tag{2}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{3}$$

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

$$\frac{d\ln K}{dT} = \frac{\Delta H^{\circ}}{RT^2} \tag{4}$$

where K, T and R represent, respectively, the equilibrium constant, the operating temperature and the gas constant, and ΔH° 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:

$$\prod_i (y_i\phi_i)^{\upsilon_i} = \left(\frac{P}{P^0}\right)^{-\upsilon} K \tag{5}$$

$$\upsilon = \sum_i \upsilon_i \text{ and } y_i = \frac{n_i}{\sum_i n_i} \tag{6}$$

where P, P^0, y_i and υ_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 ϕ_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:

$$K_1 = \frac{y_{CO}^2 y_{H_2}^4}{y_{C_2H_5OH} y_{H_2O}} P^4 \tag{7}$$

$$K_2 = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{H_2O}} \tag{8}$$

$$K_3 = \frac{y_{CH_4} y_{H_2O}}{y_{CO} y_{H_2}^3} P^{-2} \tag{9}$$

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

$$n_{EtOH} = a - x_1 \tag{10}$$

$$n_{H_2O} = b - x_1 - x_2 + x_3 \tag{11}$$

$$n_{H_2} = 4x_1 + x_2 - 3x_3 \tag{12}$$

$$n_{CO} = 2x_1 - x_2 - x_3 \tag{13}$$

$$n_{CH_4} = x_3 \tag{14}$$

$$n_{CO_2} = x_2 \tag{15}$$

$$n_{total} = \sum_{i-1}^{6} n_i = a + b + 4x_1 - 3x_2 \tag{16}$$

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.