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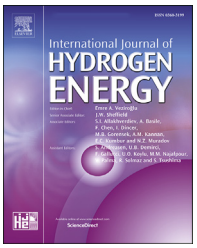

Theoretical study of hydrogen production by ethanol steam reforming: Technical evaluation and performance analysis of catalytic membrane reactor

Majid Saidi [a,*], *Alireza Jahangiri* [b]

[a] School of Chemistry, College of Science, University of Tehran, PO Box 14155-6455, Tehran, Iran
[b] Faculty of Engineering, Shahrekord University, Shahrekord, Iran

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ABSTRACT

Ethanol steam reforming over a Co/Al_2O_3 catalyst was studied theoretically in a catalytic Pd–Ag membrane reactor (CMR). A mathematical model has been developed to elucidate the behavior of CMR by taking into account the chemical reactions, heat and mass transfer phenomena. The effect of operating parameters on the performance of CMR has been evaluated in terms of ethanol conversion, hydrogen recovery and hydrogen yield. The results revealed the high performance of this configuration is related to the continuous removal of hydrogen from the retentate side, shifting the reaction equilibrium towards hydrogen formation. Sensitivity analysis of operating parameters indicate that ethanol conversion is favored at higher temperatures, pressures, sweep ratios and feed molar ratios. Moreover, increasing the feed molar ratio enhances the ethanol conversion, and decreases the hydrogen recovery due to reduction of partial pressure of hydrogen and consequently decreasing the driving force for the hydrogen permeation through the membrane.

Introduction

Because of growing energy demands associated with the increasing greenhouse effect, interest in the application of renewable energy resources has enhanced significantly all over the world [1–4]. Hydrogen can be used as a clean and highly efficient energy carrier [5–7]. Currently, hydrogen is produced from fossil fuels such as methane, which involves CO and CO_2 as a byproduct of conversion processes [8,9]. Recently, due to depletion of fossil fuels and environmental considerations, there is a growing interest to produce hydrogen from renewable alternatives such as alcohols [5,10–15]. Indeed, biomass can be converted to intermediate bio–fuels such as pyrolysis oil, biogas, methanol and ethanol. In particular, among the various alcohol feedstocks, bio–ethanol is used extensively as an efficient and prevalent source for hydrogen production due to its higher H/C ratio, lower volatility and toxicity, higher safety and easy handling [11,14,16–21]. Also, bio–ethanol is considered as a clean fuel in terms of composition and easy production by fermentation of biomass such as waste materials and forestry residue.

* *Corresponding author.*
E-mail addresses: majid.saidi@khayam.ut.ac.ir, majid.saidi@ut.ac.ir (M. Saidi).
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Ethanol steam reforming (ESR) is a highly endothermic reversible reaction, therefore from the thermodynamic viewpoint, ESR is favored at high temperature, low pressure and low space velocity. The ESR can be described by the reaction (R–1). Additionally, side reactions such as water gas shift reaction (WGS) can occur affecting the equilibrium and producing non–desirable byproducts. Also, it is well known that hydrogen can be produced through thermal decomposition of ethanol (ED), (R–3) [10,14,22].

$$\textit{Ethanol Steam Reforming}: \quad C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2 \qquad \Delta H_{298K} = 157.09 \quad kJ\cdot mol^{-1} \tag{R-1}$$

$$\textit{Water} - \textit{Gas Shift Reaction}: \quad CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -41.19 \quad kJ\cdot mol^{-1} \tag{R-2}$$

$$\textit{Ethanol Decomposition}: \quad C_2H_5OH \leftrightarrow CH_4 + CO + H_2 \qquad \Delta H_{298K} = 33.18 \quad kJ\cdot mol^{-1} \tag{R-3}$$

The efficiency of ESR process can be determined by various factors such as ethanol conversion, hydrogen recovery and hydrogen yield. The process efficiency is dependent on various parameters including operating conditions, catalyst type and especially reactor configuration. Traditional reactors such as packed, fixed, moving and fluidized beds have been widely used as one of the most applicable reactors for ESR due to easy application and installation, simplicity of structure and low construction and operating cost. However recent research revealed that they have lower efficiency with respect to other new types such as catalytic membrane reactors (CMR). Gallucci et al. [10] compared the performance of CMRs with respect to traditional packed bed reactors, and investigated the influence of operating conditions on the ethanol conversion and pure hydrogen production in a dense Pd–Ag membrane reactor. Their results indicated that application of CMR technology improves the ethanol conversion. In another related investigation, De Falco [23] studied the methane steam reforming (MSR) in a Pd-based membrane reactor and observed a twofold methane conversion with respect to a traditional reformer. Also, Iulianelli et al. [24] evaluated MSR in a dense Pd–Ag membrane reactor and observed similar conversion to the packed bed reactor. Different palladium–based membranes as a particular type of CMR technology have been applied under industrial conditions representing an excellent performance due to high hydrogen perm–selectivity. In the membrane reactor technology, the constant removal of H_2 from the reaction side leads to higher conversions.

Techno–economic evaluation of energy systems revealed that application of CMR can be beneficial under specific market and regulatory conditions. CMR as a novel configuration can significantly improve the ethanol conversion and hydrogen production by simultaneous integrating the reaction and separation processes in one unit. In the CMR technology, ESR process takes place over the catalyst in the reaction zone (tube side) and hydrogen permeates through the membrane to the shell side. Continues selective removal of hydrogen through the membrane shifts ESR equilibrium conditions towards the desired products. Past research indicate that Co–based catalysts produce higher H_2 fluxes due to their high activity and selectivity [14,25]. Different types of Co and Co–alloy catalytic membranes have been evaluated under experimental or pilot conditions, representing an appropriate performance for their application in industrial–scale. As reported in the literature, Co–based catalysts can operate at lower temperatures with respect to noble metal–based catalysts [25–30]. As a result, Co–based catalysts do not yield methane as an intermediate product, which can only be formed at elevated temperatures. Based on presented mechanism for ESR over Co–based catalyst, ethanol is dehydrogenated into a mixture of H_2 and acetaldehyde and subsequently, acetaldehyde reacts with steam to yield mainly H_2 and CO_2 [25,30]. Therefore the most important advantage of conducting ESR at lower temperatures is that the WGS equilibrium favors the formation of H_2 and CO_2 and maximize production of H_2.

This research focuses mainly on evaluating and analyzing the performance of CMR for pure hydrogen production via the ESR over a Co/Al_2O_3 catalyst at a wide range of operating conditions, including 573–973 K, 2–16 bar, the sweep ratio of 1–10 and the feed molar ratio (H_2O/C_2H_5OH) of 2–12. Consistently process modeling of ESR is an important step for design, scale–up and optimization of industrial hydrogen production plants. Therefore, the main objective of this study is to develop a clear understanding of the effects of various design and operating parameters on the ethanol conversion, H_2 recovery and total hydrogen yield. A two–dimensional non–isothermal stationary mathematical model is developed to investigate the behavior of CMR by considering the main chemical reactions, heat and mass transfer phenomena, where they play a crucial role in the performance of the process. In comparison with previous related studies, the present model can provide important insights into the role of hydrogen flux through the membrane, diffusion and thermal conductivity in the radial direction. Also, thermal analysis is performed and temperature profiles are predicted. The ability of the present constructed model to calculate and predict the trends in the data should help to provide a reliable situation for understanding and developing the optimal design for hydrogen production in the industrial scale.

Kinetic assessment

Since (R–1) and (R–3) are reversible and endothermic reactions, and based on Le Chatelier's principle, increasing the temperature and decreasing the pressure improve ethanol conversion. In the present work, the kinetic analysis of the ESR process in the CMR, is carried out based on developed model by Sahoo et al. [14]. The rates of these reversible reactions are expressed as:

$$r_{ESR} = \frac{k_{ESR}\cdot K_{CH_3CH_2O(1)}\cdot\left(\frac{p_{CH_3CH_2O}}{p_{H_2}^{1/2}}\right)\cdot\left[1-\left(\frac{p_{H_2}^4\cdot p_{CO_2}^2}{K_{ESR}^*\cdot p_{CH_3CH_2O}\cdot p_{H_2O}^2}\right)\right]}{S}\left(C_{S_1}^T\right)^2 \tag{1}$$

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