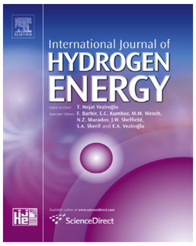
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–17

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Modelling and sequential simulation of multi-tubular metallic membrane and techno-economics of a hydrogen production process employing thin-layer membrane reactor

Alireza Shafiee [a], Mobin Arab [a], Zhiping Lai [b], Zongwen Liu [a], Ali Abbas [a],*

[a] School of Chemical and Biomolecular Engineering, The University of Sydney, Sydney, Australia
[b] Advanced Membranes and Porous Materials Center, Chemical and Biological Engineering, Division of Physical Science and Engineering, King Abdullah University of Science and Technology, Thuwal, 23955, Saudi Arabia

ARTICLE INFO

Article history:
Received 10 February 2016
Received in revised form
26 August 2016
Accepted 26 August 2016
Available online xxx

Keywords:
Hydrogen
Membrane reactor
Palladium membrane
Natural gas reforming
Gas separation
Techno-economic modelling

ABSTRACT

A theoretical model for multi-tubular palladium-based membrane is proposed in this paper and validated against experimental data for two different sized membrane modules that operate at high temperatures. The model is used in a sequential simulation format to describe and analyse pure hydrogen and hydrogen binary mixture separations, and then extended to simulate an industrial scale membrane unit. This model is used as a subroutine within an ASPEN Plus model to simulate a membrane reactor in a steam reforming hydrogen production plant. A techno-economic analysis is then conducted using the validated model for a plant producing 300 TPD of hydrogen. The plant utilises a thin (2.5 μm) defect-free and selective layer ($Pd_{75}Ag_{25}$ alloy) membrane reactor. The economic sensitivity analysis results show usefulness in finding the optimum operating condition that achieves minimum hydrogen production cost at break-even point. A hydrogen production cost of 1.98 $/kg is estimated while the cost of the thin-layer selective membrane is found to constitute 29% of total process capital cost. These results indicate the competetiveness of this thin-layer membrane process against conventional methods of hydrogen production.

Introduction

Hydrogen is one of the most promising alternatives to traditional fossil fuels because it is a versatile energy carrier with significantly higher energy value than other commonly used fuels (Hydrogen 142 MJ/kg, methane 55.5 MJ/kg, Gasoline 44.4 MJ/kg, Bituminous Coal 24 MJ/kg) [1,2]. There has been an increasing demand for hydrogen during the past few decades [3]. This important gas is mainly produced via two processes: electrolyzing water and reforming fossil fuels. Considering the high energy requirements and costs of water electrolysis, hydrogen is mainly produced via steam reforming or partial oxidation of hydrocarbons [4]. One of the most important hydrogen production technologies is steam methane reforming (SMR) in which syngas (a mixture of H_2 and CO) is

---

* *Corresponding author*. Fax: +61 2 9351 2854.
E-mail address: ali.abbas@sydney.edu.au (A. Abbas).

http://dx.doi.org/10.1016/j.ijhydene.2016.08.172

Nomenclature

N_i	mass transfer flux of component i
A	membrane area
P_{fb_i}	bulk partial pressures of feed for component i
P_{pb_i}	bulk partial pressures of permeate for component i
RES	overall mass transfer resistance
$\overline{P_i}$	permeability of component i over the membrane
δ	membrane thickness
Kmi	permeance of component i over the membrane
K_s	Sieverts' constant
ΔG_R^0	standard Gibbs free energy of the reaction
ΔS_R^0	standard entropy of the reaction
ΔH_R^0	standard enthalpy of the reaction
D_i	diffusion coefficient of component i over the membrane
$\tilde{P}_{H_2}$	modified hydrogen permeability
$\tilde{K}_{H_2}$	modified hydrogen permeance
F_f	feed flow rates
F_p	permeate flow rates
x_i	molar fractions of component i in feed
y_i	molar fractions of component i in permeate
R_o	outer radius of membrane tubes
R_{in}	inner radius of membrane tubes
L	length of membrane tubes
N	total number of membrane tubes
R	ideal gas constant
T	temperature of gas mixture
μ_m	gas mixture viscosity
γ	specific heat ratio
Q	gas volume flow rate
K	reaction rate coefficient
E	activation energy

produced [5,6]. This coupled with the development and exploitation of rich natural gas resources has led to substantial attention towards improving the yield of syngas in the SMR process [7].

Reforming of natural gas comprises of two reversible reactions driven by thermodynamic equilibrium: an endothermic reforming reaction (i.e. $CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$) and an exothermic water gas shift (WGS) reaction (i.e. $CO + H_2O \rightleftharpoons CO_2 + H_2$). Selective removal of produced hydrogen, e.g. through a membrane separation, affects the reactions equilibrium and shifts the reactions towards hydrogen production. Consequently, methane conversion rate increases. Therefore, simultaneous production and separation of hydrogen intensifies the process into a simpler and more compact reaction-separation design. However, separation of hydrogen, from other gases such as CO, CO_2, CH_4 and H_2O, remains a significant technical and economic barrier. The membrane reactor (MR), as a novel reforming technology which is under development, promises economic small-scale hydrogen production [8]. Using MRs, the same hydrogen yield is achievable at milder conditions and at higher hydrogen purity compared to that of conventional reactors [9]. Numerous experimental and theoretical studies have investigated the thermodynamics of the MRs for the SMR process (SMR-MR) [10–14]. Importantly, it has been reported that relatively higher fuel conversion can be achieved in MRs at temperatures lower than those of conventional technology [14,15].

In the context of hydrogen separation, metallic membranes are an attractive option due to their infinite selectivity and relative high permeability for hydrogen over other species [16]. Only hydrogen is able to pass through a variety of dense metals through interstitial diffusion mechanism. This is due to the small interstitial site size as well as structures of metals such as pure metals, crystalline alloys and amorphous alloys that can be considered as membranes for hydrogen purification. The hydrogen permeable metals have a distinct specification for gas separation which is a function of the crystal lattice structure, chemical reactivity and lattice defects [17]. In addition, metallic membranes are highly compatible with high-temperature applications [18]. Membranes made of Group 10 metals (i.e. nickel, palladium, and platinum) are noticeably more active toward dissociation and dissolution of hydrogen. Palladium membranes have a supreme ability to carry hydrogen through their metallic structure due to the high bulk solubility of hydrogen over a wide temperature range [19]. Hence, Pd-based membrane has become one of the most studied metallic membranes in separation and purification of hydrogen [20].

Despite of published works on technical feasibility of using thin selective defect free layer Pd based hydrogen membranes [21–24] and the importance of Pd based membrane thickness in hydrogen production [25], no detailed economic analysis on using a thin selective layer industrial Pd based SMR-MR were found in literature. As such, studying such processes more holistically and from a systems techno-economic perspective is necessary for better estimation of the membrane cost contribution. Therefore, in this paper, we considered use of thin Pd-based membranes here to provide a more holistic view of economics of SMR-MR.

Deploying fundamental and precise MR model seems necessary to perform analysis with acceptable accuracy. However, coupling a selective membrane separation process with chemical reactions and mass transfer on both sides of reactor in MR, presents interesting challenges [26–29]. During past decades there has been numerous theoretical attempts to model MRs based on different assumptions and for different membrane configurations [9,28,30–33]. But, these models have been under restriction of considered assumptions and operating parameters and there is no developed single validated SMR-MRs model [34]. The proposed reactor models are categorized according to their number of dimensions into one, two and three dimensional models [35]. Where gradient in axial direction is negligible, one dimensional model is simple and frequently used for MR modelling [34–36]. Marin et al. and Oyama and Hacarlioglu in separate works simulated and compared the performance of some plug membrane reactor models. They made a suggestion criterion for selecting different models in different operating conditions and studied the effect of the different operating conditions on performance of MRs [37,38]. Through various proposed models,

Please cite this article in press as: Shafiee A, et al., Modelling and sequential simulation of multi-tubular metallic membrane and techno-economics of a hydrogen production process employing thin-layer membrane reactor, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.08.172