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ORIGINAL ARTICLES

# Ultra-clean hydrogen production by ammonia decomposition

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**KEYWORDS**

Ammonia decomposition;
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**Abstract** A rigorous heterogeneous mathematical model is used to simulate a cascade of multi-stage fixed bed membrane reactors (MSFBMR) with inter-stage heating and fresh sweep gas for the decomposition of ammonia to produce high purity hydrogen suitable for the PEM fuel cells. Different reactor configurations are compared. The comparison between a single fixed bed reactor (FBR) and a single fixed bed membrane reactor (FBMR) shows that the FBMR is superior to the FBR and gives 60.48% ammonia conversion higher than the FBR. However, 20.91% exit ammonia conversion obtained by the FBMR is considered to be poor. The FBMR is limited by the kinetics at low temperatures. The numerical results show that the MSFBMR of four beds achieve 100.0% ammonia conversion. It was found that the membrane plays the prime role in the displacement of the thermodynamic equilibrium. The results also show that, a linear relationship exists between the number of beds and the feed temperature and a correlation has been developed. A critical point for an effective hydrogen permeation zone has been identified. It is observed that the diffusion limitation is confined to a slim region at the entrance of the reactor. It is also observed that the heat load assumes a maximum inflection point and explanations offered. The results show that the multi-stage configuration has a promising potential to be applied successfully on-site for ultra-clean hydrogen production.


## 1. Introduction

Ultra-clean hydrogen has been recognized as a carbon-free fuel that can be used to power polymer electrolyte membrane (PEM) fuel cells. The PEM fuel cell is an efficient electrochemical device that produces electricity that can be used in several important applications such as transportation, power generation and electronic devices (Zamel, 2013). Although the PEM fuel cells are a versatile clean technology and friendly to the environment, but are sensitive to hydrogen purity. Carbon monoxide traces of about (5–10 ppm) are enough to severely poison the active sites of the platinum catalyst at the anode, resulting in transient cell potential oscillations and a profound drop in the overall efficiency of the PEM fuel cell (Oetjen et al., 1996; Farrell et al., 2007). Also, ammonia traces of about 13 ppm have catalyst poisoning effects on the PEM

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**Nomenclature**

| | |
|---|---|
| $A_o$ | reactor area, $m^2$ |
| $C$ | total concentration, kmol/$m^3$ |
| $C_i$ | concentration of component $i$, kmol/$m^3$ |
| $C_{pi}$ | specific heat of component $i$, kJ/kmol K |
| $C_{pmix}$ | gas specific heat, kJ/kg °C |
| $d_{H2}$ | diameter of hydrogen membrane tube (m) |
| $D_i$ | bulk diffusion coefficient of component $i$, $m^2$/h |
| $D_i^o$ | diffusion coefficient of component $i$ at 0 °C and 1 atm, $m^2$/h |
| $D_{ji}^o$ | diffusion coefficient of component $j$ in component i, $m^2$/h |
| $D_{ei}$ | effective diffusion coefficient of component $i$, $m^2$/h |
| $f_i$ | fugacity of component $i$ |
| $F_i$ | molar flow rate of component $i$, kmol/h |
| $F_i^o$ | initial molar flow rate of component $i$, kmol/h |
| $\Delta H$ | enthalpy change of reaction, kJ/kmol |
| $K$ | equilibrium constant, $kPa^{-1}$ |
| $K_{ea}$ | effective axial dispersion coefficient, m/s |
| $K_{er}$ | effective radial dispersion coefficient, m/s |
| $L$ | length of the bed, m |
| $\dot{m}_{mix}^j$ | mass flow rate of the mixture at heat exchange $j$, kg/h |
| $N_i$ | molar flux of component $i$ in $r$ direction, kmol/$m^2$. s |
| $N_{bed}$ | number of beds |
| $P$ | total pressure, kPa |
| $P_i$ | partial pressure of component $i$, kPa |
| $Q_j$ | heat load of heat exchanger $j$, kW |
| $r$ | radial coordinate of spherical catalyst pellet, m |
| $r_1$ | radial dimension in catalyst bed, m |
| $r_2$ | radial dimension in ceramic support, m |
| $R$ | university gas constant, kJ/kgmol.K |
| $R_1$ | inner tube radius, m |
| $R_2$ | outer radius of composite tube, m |
| $R_p$ | radius of spherical pellet, m |
| $R_{NH3}$ | reaction rate of ammonia decomposition, kmol/h $m^3$ |
| $T$ | temperature, K |
| $T_j$ | inlet temperature of heat exchanger $j$, °C |
| $T_f$ | feed temperature, °C |
| $u_l$ | axial velocity, m/s |
| $V$ | reactor volume, $m^3$ |
| $X_i$ | mole fraction of component i inside catalyst pellet |
| $Y_i$ | mole fraction of component $i$ |
| $Z$ | ammonia conversion |

*Greek letters*

| | |
|---|---|
| $\alpha$ | kinetic parameter |
| $\gamma_i$ | generalized stoichiometric coefficient of component $i$ |
| $\delta$ | thickness of hydrogen membrane, μm |
| $\varepsilon$ | porosity of catalyst pellet |
| $\varepsilon_1$ | porosity of catalyst bed |
| $\varepsilon_2$ | porosity of ceramic support |
| $\rho_{mix}$ | gas density, kg/$m^3$ |
| $\eta$ | effectiveness factor |
| $\lambda$ | intraparticle porosity |
| $\phi_i$ | fugacity coefficient of component $i$ |
| $\omega$ | dimensionless radial coordinate of spherical catalyst pellet |

*Subscripts*

| | |
|---|---|
| $f$ | feed |

*Superscripts*

| | |
|---|---|
| $B$ | bulk |
| $c$ | ceramic support |
| $p$ | pellet |
| $s$ | shell side |
| $t$ | tube side |

fuel cells (Uribe et al., 2002; Chellappa et al., 2002; Vilekar et al., 2012). Conventional steam reformers produce inevitably hydrogen with carbon monoxide beyond allowable limits. Therefore, the purity of hydrogen imposes severe constraints on the conventional hydrogen production processes.

In recent years, it has been shown that the implementation of hydrogen perm-selective composite membranes in the new reformer generations have a greater role in solving the problem of hydrogen purity as well as hydrogen yield by selective hydrogen separation and displacement of thermodynamic equilibrium (Collins et al., 1993; Collins and Way, 1993; Hughes, 2001; Dittmeyer et al., 2001; Abashar, 2002; Abashar et al., 2002; Abashar, 2015; Buxbaum and Lei, 2003; Liang and Hughes, 2005; Garcia et al., 2008). However, high pressure driving forces are needed for hydrogen permeation. Further improvements in production, efficient design and operation of these reformers are still needed.

The challenges facing utilization of ultra-clean hydrogen fuel are transportation, delivery, distribution and storage (Alagharu et al., 2010; Di Carlo et al., 2011, 2014; Chiuta et al., 2013). Hydrogen in the gas form requires high pressure vessels (70 MPa) and in a cryogenic liquid form (−253 °C) requires expensive insulated tanks (Zuttel, 2004; Di Carlo et al., 2011). Recently, the on-site (local) hydrogen production and supply has received much attention (Chellappa et al., 2002; Zuttel, 2004; Waghode et al., 2005; Chein et al., 2010; Chiuta et al., 2013; Rizzuto et al., 2014). Liquid methanol (12.50 mass% $H_2$) and ammonia (17.65 mass% $H_2$) are competent candidates for the on-site hydrogen production due to their attractive characteristics (high energy density, fewer storage problems, ...etc.) (Metkemeijer and Achard, 1994; Di Carlo et al., 2011). However, reforming of methanol suffers from the problem of carbon oxides (Di Carlo et al., 2014). On the other hand, ammonia is a carbon free compound and in a single step the thermal cracking only gives hydrogen and nitrogen. Moreover, ammonia decomposition process is an economical hydrogen process more than the methanol process (Garcia et al., 2008; Di Carlo et al., 2014). Another attractive

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