Ultra-clean hydrogen production by 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...
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; Garcia et al., 2008). However, their attractive characteristics (high energy density, fewer storage problems, ...etc.) (Metkemeijer and Achard, 1994; Di Carlo et al., 2011). 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; Abashar et al., 2011). However, reforming of methanol suffers from the problem of carbon oxides (Di Carlo et al., 2014). Liquid methanol (12.50 mass% H2) and ammonia (17.65 mass% H2) are competent candidates for the on-site hydrogen production due to their attractive characteristics (high energy density, fewer storage problems, ...etc.) (Abashar et al., 2013). Liquid methanol and ammonia decomposition process is an economical hydrogen process more than the methanol process (Garcia et al., 2008; Di Carlo et al., 2014). Another attractive
property of ammonia is lower production cost (1 S/kg) compared with hydrogen (3.5–5.5 S/kg) (Di Carlo et al., 2011). These characteristics grant privilege to ammonia.

Previous theoretical studies on the ammonia decomposition are focused on the removal of toxic ammonia traces as a pollutant (Gobina et al., 1995; Abashar, 2002; Abashar et al., 2002). Remarkable efforts have been done to improve the performance of the catalysts used in ammonia synthesis and decomposition such as iron, nickel, ruthenium (Yin et al., 2004; Cooper and Botte, 2006; Hellman et al., 2009). However, theoretical studies on using ammonia as a feedstock for hydrogen production are limited (Chen et al., 2010) and the modeling and numerical simulation are conducted at the level of experimental bench scale reactors (Sorensen et al., 2006; Chen et al., 2010; Di Carlo et al., 2011, 2014; Rizzuto et al., 2014). More studies are needed for the pilot plants and full scale reactors.

Theoretical studies of multi-stage membrane reactors for the decomposition of ammonia are surprisingly scarce. This study is conducted to gain insight and understanding of ammonia decomposition such as iron, nickel, ruthenium (Yin et al., 2002). Remarkable efforts have been done to improve the performance of different reactor configurations. Furthermore, the effects of the key parameters on the performance of the MSFBMR configuration are considered.

2. Reaction kinetics

The decomposition of ammonia is a single step endothermic reaction as follows:

\[ \text{NH}_3 = \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 [\Delta H_{298} = 54.6 \text{ kJ/mol}] \] (1)

The reaction rate of ammonia decomposition is given by the following Temkin form (Temkin and Pyzhov, 1940; Dyson and Simon, 1968; Singh and Saraf, 1979; Elnashaie et al., 1988):

\[ R_{\text{NH}_3} = 5.131 \times 10^{14} \exp \left( \frac{-19656.27}{T} \right) \times \left[ \frac{f_i}{f_{\text{NH}_3}} \right]^* - K^2 f_{\text{N}_2} \left( \frac{f_i}{f_{\text{NH}_3}} \right)^{1-x} \] (2)

where \( f_i \) is the fugacity of component \( i \) and is given by:

\[ f_i = \phi_i Y_i P \] (3)

where \( \phi_i \) is the fugacity coefficient of component \( i \), \( Y_i \) is the mole fraction of component \( i \) and \( P \) is the total pressure. The equilibrium constant is given as follows:

\[ \log K = 2.6899 + 2011.6 \times T^{-1} + 1.848863 \times 10^{-7} T^2 - 2.691122 \log T - 5.519265 \times 10^{-5} T \] (4)

where \( T \) is the absolute temperature (K).

3. Model development

A two-dimensional model is developed for the decomposition of ammonia. Schematic diagrams of a single fixed bed membrane reactor (FBMR), a cascade of multi-stage fixed bed membrane reactors (MSFBMR) with inter-stage heating and fresh sweep gas. And, also experimental bench scale reactors (Sorensen et al., 2006; Chen et al., 2010; Di Carlo et al., 2011, 2014; Rizzuto et al., 2014). More studies are needed for the pilot plants and full scale reactors.

The differential mass balance equations on component \( i \) gives:

\[ \frac{\partial C_i^r}{\partial V} = \frac{D_{i,i}^r}{A_i} \frac{1}{r_1} \frac{\partial}{\partial r_1} \left[ r_1 \frac{\partial C_i^r}{\partial r_1} \right] + \frac{(1 - \epsilon_i) \gamma_i R_{\text{NH}_3}}{A_i h_l} \quad 0 < r_1 < R_l, \quad i = 1 \text{ to } 3 \] (5)

where \( i = 1, 2 \) and 3 for \( \text{NH}_3, \text{N}_2, \) and \( \text{H}_2 \), respectively. \( \gamma_i \) is the generalized stoichiometric coefficient of component \( i \) (negative for reactants).

The boundary conditions are:

\[ V = 0 \quad C_i^l = C_i^l \] (6)

\[ r_1 = 0 \quad \frac{\partial C_i^r}{\partial r_1} = 0, \quad i = 1 \text{ to } 3 \] (7)

\[ r_1 = R_l \quad C_i^r = C_i^r \] (8)

The effective diffusivity coefficient is calculated from:

\[ D_{ij} = \frac{(1 - \epsilon_i)}{\sum_{j=1}^n (Y_j/D_{ij})} \] (9)

3.1. Tube side

The differential mass balance equations on component \( i \) is given by:

\[ \frac{D_{i,i}^r}{r_2} \frac{\partial}{\partial r_2} \left[ r_2 \frac{\partial C_i^r}{\partial r_2} \right] = 0, \quad R_l < r_2 < R_2, \quad i = 1 \text{ to } 3 \] (10)

The boundary conditions are:

\[ r_2 = R_l \quad C_i^r = C_i^r \] (11)

\[ \frac{\partial C_i^r}{\partial r_2} \bigg|_{r_2=R_2} = 0, \quad i = 1, 2 \] (12)

for \( \text{H}_2 \):

\[ \frac{\partial C_i^r}{\partial r_2} \bigg|_{r_2=R_2} = \left( \frac{28.84 \times 10^{-5}}{T} \right) \left[ \sqrt{P_{\text{H}_2}^i} - \sqrt{P_{\text{H}_2}} \right] \] (13)

and energy balance equation is given by:

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The boundary conditions are:

\[ V = 0 \quad T = T_f \]
\[ V = V_o \quad \frac{\partial T}{\partial V} = 0 \]
\[ r_1 = 0 \quad \frac{\partial T}{\partial r_1} = 0 \]
\[ r_1 = R_1 \quad \frac{\partial T}{\partial r_1} = 0 \]

The conversion of ammonia is given by:

\[ Z = 1 - \frac{F_{NH_3}}{F_{NH_3}} \]

3.3. Catalyst pellet and effectiveness factor

A differential molar balance inside a porous catalyst pellet on component \( i \) gives:

\[ \frac{1}{r^2} \frac{d}{dr} (r^2 N_i) = \nu_i \frac{R_{NH_3}(X_i, T, P)}{(1 - e)} \]

subject to boundary conditions:

Figure 1 Schematic representation: (a) single fixed bed membrane reactor (FBMR); (b) multi-stage fixed bed membrane reactors (MSFBMR); (c) differential element in the membrane reactor.
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\[ r = 0 \quad N_i = 0 \]
\[ r = R_p \quad X_i = X_i^0 \]  

Using lengthy manipulation, the following intraparticle dimensionless molar balance equation for the catalyst pellet is obtained:

\[
\frac{d^2X_i}{d\sigma^2} + \frac{2}{\omega} \frac{dX_i}{d\sigma} = \frac{1}{(\sigma_i - 1)} \left( \frac{dX_i}{d\sigma} \right)^2
= -\gamma_i \frac{R_p^2}{D_i} \left( 1 - \frac{X_i}{\gamma_i} \right) \frac{R_{NH3}(X_i, T, P)}{(1 - \varepsilon)}
\]  

with boundary conditions as:

\[ \omega = 0 \quad \frac{dX_i}{d\sigma} = 0 \]
\[ \omega = 1 \quad X_i = X_i^b \]  

where \( \omega (\omega = r/R_p) \) is the dimensionless coordinate, \( C \) is the total concentration and \( D_i \) is the effective diffusion coefficient of component \( i \). The effective diffusion coefficient is given by (Elnashaie et al., 1988):

\[ D_i = \frac{1}{2} \varepsilon D_i \]  

where \( \varepsilon \) is the intraparticle porosity and \( D_i \) is bulk diffusion coefficient of component \( i \). The bulk diffusion coefficient is given by:

\[ D_i = D_i^b \left( \frac{T}{273} \right)^{1.75} \frac{1}{P} \]  

The diffusion coefficient of component \( i \) \( (D_i^b) \) at 0 °C and 1 atm is given by:

\[ D_i^b = \frac{1}{\sum_{i=1}^{N} (X_i^b/D_i^b) - (X_i^b/D_i^b)} \]  

and \( X_i \) is given by:

\[ X_i = \gamma_i - (\gamma_i - X_i^b) \frac{\gamma_i - X_i}{\gamma_i - X_i^b} \]  

The effectiveness factor is used as a measure of diffusion resistances inside the catalyst pellet and defined as the actual overall rate of reaction divided by the rate of reaction at the bulk (surface) conditions.

\[ \eta = \frac{\int_{0}^{R_p} r^2 R_{NH3}(X, T, P)dr}{\int_{0}^{R_p} r^2 R_{NH3}^b(X^b, T^b, P^b)dr} \]  

where \( X \) is the vector of mole fractions, \( X^b \) is the vector of mole fractions at the bulk conditions and \( R_p \) is the radius of the catalyst pellet.

### 3.5. Inter-stage heat load

The inter-stage heat load per \( j \) heat exchanger is calculated by the following equation:

\[ Q_j = \eta_m c_p \left( T_f - T_j \right) \]  

The cumulative heat load is the sum of the inter-stage heat loads \( (\sum Q_j) \).

### 4. Solution algorithm

Data for simulation are presented in Table 1. The global orthogonal collocation technique (Villadsen and Michelsen, 1978) is implemented to change the set of the partial differential into a set of ordinary equations. Then, the new set of ordinary differentials is integrated by an IMSL subroutine (DGAR) based on a Runge–Kutta–Verner fifth and sixth-order method with automatic step size and double precision to ensure accuracy. The two-point boundary value differential equations of the catalyst pellet are discretized by the global orthogonal technique to give a set of nonlinear algebraic equations. These nonlinear algebraic equations are solved numerically by an IMSL subroutine called ZSPOW. A special technique has been applied for the initial guesses to ensure the convergence of the equations to the desired level of accuracy. The technique started from one collocation point and the solution of the one collocation point is utilized to find the initial guesses for the two collocation points and so on. Three collocation points are adopted in this study, since more than three collocation points give almost the same profiles inside the catalyst pellet.

### 5. Results and discussion

According to Le Châtelier’s principle the position of a chemical equilibrium is controlled by the changes of concentration, pressure and temperature. In the case of ammonia decomposition, the reaction is endothermic and reversible with increasing number of moles. Hence, the ammonia equilibrium conversion increases with increase of temperature, decrease of pressure and removal of products. Moreover, the increase of temperature also has a positive effect on the kinetics by increasing the rate of ammonia decomposition. Hence, for a reactor without membrane it is desirable to work at low pressures and high

<table>
<thead>
<tr>
<th>Feed composition</th>
<th>Mol%</th>
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<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td>95.00</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>3.00</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>2.00</td>
</tr>
</tbody>
</table>

**Reactor**

| Volume of the catalyst bed (m²) | 0.1 |
| Diameter of bed (m) | 0.2 |
| Membrane thickness (µm) | 3.0 |
| Diameter of catalyst pellet (m) \( 3.0 \times 10^{-3} \) | |
| Void fraction | 0.46 |
| Pressure of sweep gas stream (bar) | 1.0 |

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temperatures. However, excessive temperatures have destructive effects on the catalyst and the reactor. In the case of the membrane reactor the increase of pressure has two opposing effects of shifting the equilibrium to the right by enhancing the permeation of hydrogen and to the left by decreasing the number of moles to form ammonia. Therefore, the direction of the equilibrium is controlled by the dominant force.

In this study the single reactor configuration is considered first. Fig. 2a shows exit ammonia conversion as a function of pressure obtained by a single fixed bed membrane reactor (FBMR). The profile shows a minimum value at \( P = 8.342 \) bar due to the two competing forces. It is clearly shown that, the exit ammonia conversion decreases with the increase of the pressure due to its negative influence on the thermodynamic equilibrium to a critical inflection point beyond which the role of the membrane comes to dominate and developing an effective permeation zone. As it can be seen that the operating pressure must be in the effective permeation zone i.e. \( P > 8.342 \) bar. The operating pressure selected for this study is 40.0 bar around the value given by Rahimpour and Asgari (2009). Note that this critical point needs to be identified at various operating conditions to determine the critical minimum operating pressure.

In order to select an appropriate reactor volume throughout this study, the rate of ammonia reaction in the fixed bed membrane reactor (FBMR) at 40.0 bar is presented in Fig. 2b. As it can be seen in Fig. 2b, that the reaction is very fast and the rate of ammonia reaction drops drastically to a low value. This figure shows that the part of reactor beyond 0.1 m\(^3\) seems to have an insignificant effect. Therefore, a reactor volume of 0.1 m\(^3\) is adopted in the rest of this study.

Fig. 3a compares the performance of a single fixed bed reactor (FBR) and a fixed bed membrane reactor (FBMR). It is clearly shown that the exit ammonia conversion is significantly enhanced by the FBMR i.e. the exit ammonia conversion is increased by 60.48% from 13.03% obtained by the FBR to 20.91% obtained by the FBMR. Despite the fact that the membrane plays the main role in the displacement of the thermodynamic equilibrium and achieving a high ammonia conversion, at the same time causing a severe drop in temperature along the length of the reactor as shown in Fig. 3b. The drop in the temperature has a negative effect on the kinetics and limited further improvement in the exit ammonia conversion.

Fig. 3c shows hydrogen concentration profiles along the length of the FBR and FBMR. A build up of hydrogen concentration along the FBR is shown, while a drastic drop in hydrogen concentration occurs along the length of the FBMR due to hydrogen permeation. It seems that the hydrogen perm-selective membrane is very effective in removing hydrogen from the reaction media and displacement of the thermodynamic equilibrium. The comparison also shows that the reactor product from the FBMR is an ultra-clean hydrogen and also high grade nitrogen products which can be used as a feedstock for other industries.

The effectiveness factor profiles along the length of the FBR and FBMR are depicted in Fig. 3d. The value of the effectiveness factor is used to indicate the magnitudes of reaction and diffusion limitations. As it can be seen in Fig. 3d that at the beginning of the reactor the effectiveness factor is low indicating that the intraparticle diffusion has a strong effect on the rate of reaction i.e. the reaction is diffusion limited. This is practically implied that the outer surface of catalyst pellet is effective. This could be due to the fast reaction at the pellet surface relative to the diffusion caused by the high feed temperature at the entrance of each bed. Then, the effectiveness factor jumps drastically to flat profiles that have a value of almost unity indicating that the reaction is limited by the kinetics at the surface of the catalyst pellet due to the low temperature at the surface. This result indicates that under the operating conditions in this study, the homogeneous model can be implemented as a good approximation without solving the catalyst pellet nonlinear two-point boundary value equations along the length of the reactor. The effectiveness factor profile for the FBMR is higher than the FBR due the fact that the surface reaction of the FBMR is less than the FBR due to the lower temperature profile as shown in Fig. 3b.

The effect of the feed temperature along the length of the FBMR is shown in Fig. 4a. A feed temperature range (600 °C–900 °C) is considered (Chiuta et al., 2013; Di Carlo et al., 2014). As shown in Fig. 4a, a substantial increase in ammonia conversion is achieved by increasing the feed temperature along the length of the reactor as shown in Fig. 4b. Note that this critical point needs to be identified at various operating conditions to determine the critical minimum operating pressure.
temperature. About 91.20% increase in ammonia conversion is obtained from 20.91% to 36.98%, when the feed temperature is increased from 600 °C to 900 °C. It is interesting to note that the effect of feed temperature on the ammonia conversion at high values is more pronounced than at low values. For example the increase of ammonia conversion is about 11.57% when the feed temperature is increased from 600 °C to 700 °C and about 32.63% when the feed temperature is increased from 800 °C to 900 °C. Fig. 4b shows the ammonia conversion as a function of temperature at different feed temperatures. As one can see that the exit low temperature in the vicinity of the equilibrium is obtained by all cases. In this situation, the performance of the FBMR is controlled by the kinetics and virtually weak hydrogen permeation. The corresponding mole fractions of the components NH₃, H₂ and N₂ are shown in Fig. 4c. The ammonia and hydrogen concentrations show inflection points of minimum and maximum value, respectively. This behavior is caused by the effect of ammonia consumption and hydrogen permeation on the total number of moles that prevail along the length of the reactor.

From the above discussion the single reactor configuration of the FBMR failed to achieve complete decomposition of ammonia due to the exit low temperature. Since the kinetics limits the performance of the FBMR at a low temperature, the idea of a multi-stage configuration (MSFBMR) with inter-stage heating is considered. In this configuration each bed has a volume of 0.1 m³. The MSFBMR configuration achieves 100% ammonia conversion by three beds and a small final bed (Bed₄) of a volume of 0.011 m³ as shown in Fig. 5a. It is obvious that this configuration works remarkably well beyond the thermodynamic equilibrium due to the imposed membrane as shown in beds 2 and 3.

Fig. 5b shows the hydrogen molar flow rate in the reaction and permeation sides for the MSFBMR configuration. As it can be shown that the hydrogen permeation is high in the first bed and decreases progressively to the last bed, this could be due to the availability of the hydrogen in the reaction side.

Fig. 6a shows the effect of the feed temperature on the number of beds that required to achieve 100% ammonia conversion. As it can be seen, that significant reduction in beds is
achieved by increasing the feed temperature. The number of the beds seems to decrease linearly with the feed temperature as shown in Fig. 6b. An empirical equation of the form is obtained:

\[ N_{\text{bed}} = \frac{C_0}{C_0 + \frac{T_f}{C_1} + 13} \]

This equation can predict satisfactorily the number of beds. In Fig. 6c the profile of heat load per interstage heat exchanger is plotted for the case of four bed configuration. In this case three interstage heat exchangers are required. The profile shows an inflection point of a maximum nature. The heat load is a function of the mass flow rate and heat capacity of the gas mixture as well as the drop of the temperature along the heat exchanger. All these quantities vary from heat exchanger to another causing this maximum point.
6. Conclusions

Ammonia decomposition is an attractive carbon free single step process for the production of hydrogen. In this paper, the conducted numerical simulation has shown that the multi-stage membrane reactors (MSFBMR) for ammonia decomposition have significant advantages over the single fixed bed membrane reactor (FBMR). Also, the MSFBMRs have attractive potential application for the efficient production of ultra-clean hydrogen suitable for the PEM fuel cells. The results suggested that the multi-stage configuration is suitable for the on-site hydrogen production. The hydrogen membrane, number of beds and the inter-stage heat exchangers strongly influenced the performance of the MSFBMR. Since, the diffusion limitations effect is shown to be confined to very small regions in each bed a pseudo-homogeneous model can be utilized as an initial trial model to extract some features of the process. The results of this preliminary study might have fundamental importance in designing of the MSFBMR for the ammonia decomposition. Optimization of this process will be addressed in future research. To this end, the compelling merits of the MSFBMR dedicate that intensive efforts are still needed in academia and industry levels.

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References


