CFD modelling of a membrane reactor for hydrogen production from ammonia

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Abstract. Despite the growing use of hydrogen (H₂) as a transport fuel, one of the major barriers still remaining is efficient and inexpensive fuel distribution and storage. Current approaches, such as compression, liquefaction or metal hydride formation, incur a significant energy penalty. Ammonia (NH₃) has long been considered a prospective H₂ medium, exhibiting a higher volumetric H₂ density than liquid H₂, through liquid-phase storage at mild pressure. Decomposition of NH₃ into H₂ and N₂ can be achieved via use of catalytic reactors and fuel-cell-grade H₂ can be produced using metal membranes at H₂ distribution sites. In this study, a 3-Dimensional (3D) Computational Fluid Dynamics (CFD) model has been developed to understand the performance of the H₂ separation process in gas mixtures derived from an NH₃-cracking reaction. The reactor consists of 19 tubular membrane tubes, each 470 mm long, inside a tubular shell with an inner diameter of 130 mm. Standard transport and energy equations governing a 3D, pressure-based, steady-state model were derived from the laws of conservation of mass, momentum and energy. The governing equations were solved using commercial CFD software ANSYS Fluent 18.0. Gas flow and mixing were modelled by the two-equation standard k-epsilon model for closure. Coupled solver was used for pressure-velocity coupling, enabling a pseudo-transient option with pseudo time steps of 0.01 s. To estimate H₂ permeation through the metal membrane, a constant H₂ permeability of 3.0E−07 mol.m⁻¹ s⁻¹ Pa⁻⁰.⁵ derived from series of experiments tested under a range of industrial conditions, was used. Model simulations were conducted for an adiabatic temperature of 300 °C, a feed-side pressure of 7.8 bar, and a permeate side pressure of 0.1 bar. A parametric analysis was carried out to explore the effects of variation in total feed-gas flow and effects of changes in NH₃-cracking efficiency on H₂ production rates and H₂ yields. The model estimated that 4.6–11.6 kg H₂/day can be produced from a 30–70 L min⁻¹ NH₃ inlet flow with 80–90% NH₃-cracking efficiency. At lower NH₃ inlet flow rates, higher H₂ yields can be obtained within a shorter distance of the membrane tubes due to relatively slower velocities and longer residence times. At high inlet flow rates, H₂ yields were significantly lower due to their faster velocities and shorter resident times, but high yields (>95%) were still observed at the membrane reactor outlet. A sensitivity analysis of the model showed that even if metal membranes functioned at only 50% of the maximum permeability, a high H₂ yield similar to that estimated using 100% permeability can still be achieved at the H₂ outlets.

1. Introduction
Hydrogen (H₂) is always considered to be a clean fuel, because it is free of carbon and does not release any CO₂ when utilised in a fuel cell or in combustion systems [1–3]. Today, the transition to a hydrogen society is led by Japan, where the number of stationary polymer electrolyte membrane fuel cells (PEMFC) deployed is around quarter of a million, and increasing dramatically [4]. The application and interest of use of H₂ as a transport fuel is also growing. However, one of the main barriers still remains: how to store and distribute H₂ in an efficient and economical way [5]. All current approaches for H₂...
storage and distribution, such as compression, liquefaction or metal hydride formation require a significant amount of energy input [6]. Alternatively, H₂ can be stored in chemicals such as ammonia (NH₃), methanol and, ethanol. Of these options, NH₃ is a very attractive option from a CO₂ aspect as it contains no carbon.

Around 200 Mt/year of NH₃ are produced globally, primarily as an agricultural fertilizer, but also for chemical production and refrigeration [5]. NH₃ also has several promising advantages for use as H₂ storage medium. NH₃ has a higher volumetric H₂ density than even liquid H₂ (120 kg/m³ c.f. 70 kg/m³), it can be easily liquefied at a mild pressure, and the volumetric energy density of liquid NH₃ is 11.5 MJ L⁻¹ which is higher than the 8.491 MJ L⁻¹ for liquid H₂ and 4.5 MJ L⁻¹ for compressed H₂ at 690 bar and 15 °C [7]; and it can be stored in solid form for convenient transportation and to limit possible toxic exposure [6, 8, 9].

The limitation of using NH₃ as an H₂ carrier is that it must be decomposed back to nitrogen and H₂ at or near to the point of use, followed by separation of the resulting H₂/N₂ mixture, as illustrated in figure 1.

![Schematic diagram of NH₃ use as a medium for H₂ storage and on-site H₂ distribution](image)

**Figure 1.** Schematic diagram of NH₃ use as a medium for H₂ storage and on-site H₂ distribution

NH₃ decomposition can be done via a catalytic NH₃-cracking reaction, as described in equation (1).

\[
\text{NH}_3 \leftrightarrow \frac{3}{2} \text{H}_2 + \frac{1}{2} \text{N}_2 \quad [\Delta H^{\circ\text{300K}} = 45.9 \text{ kJ/mol}] \quad (1)
\]

Because NH₃ decomposition is slightly endothermic, additional heat is required for the reaction. However, the associated energy penalty is comparable with compressed or liquefied H₂ [10]. The resulting gas mixture can be purified to meet ISO14687-2 and 14687-3 standards, for mobile and stationary PEM fuel cells respectively, through the use of metal membranes at the H₂ distribution sites. H₂-selective alloy membranes are an emerging technology which allows the continuous separation of H₂ mixed gas streams at elevated temperatures and pressures with potential application to a number of processes, such as natural gas reforming and coal-derived syngases processing [11, 12].

Palladium (Pd)-based alloy membranes are the clear benchmark technology, having already entered commercial production and undergone numerous long-term industrial trials. However, due to the high price of Pd, these membranes can only be commercially viable by minimising Pd consumption through developing thinner membranes and alloying with less expensive metals [12]. Vanadium (V)-based alloys are an emerging alternative to Pd membranes, and potentially offer high H₂ flux at much lower cost [12, 13]. Details of development of those alloy membranes are outside the scope of this study; here, it is sufficient to mention that V-based alloy membrane tubes were used in this study for H₂ separation from gas mixtures derived from NH₃ decomposition. Our study focused on development and simulation of a 3-dimensional (3D) computational fluid dynamics (CFD) model to understand the performance of the H₂ separation process in H₂/N₂/NH₃ gas mixtures, representing the second stage of the process described in figure 1.
2. Selecting the Reaction Level for the NH₃ Decomposition Process

Pioneering studies of the NH₃ synthesis equilibrium (the reverse reaction of equation (1)), over a large range of temperatures and pressures, were completed by Haber [15] and others. They proposed a formula to calculate a temperature ($T$)-dependent equilibrium constant ($K_p$), as shown in equation (2):

$$\log_{10} K_p = \frac{a}{T} + \beta \log_{10} T + \gamma T + \delta T^2 + I$$  \hspace{1cm} (2)

The values of $a$, $\beta$, $\gamma$, $\delta$ and $I$ can be determined from experimental data. Gillespie and Beattie [16] used a large amount of experimental data to develop these empirical parameters, thereby enabling $K_p$ to be determined for wide temperature (325–952°C) and pressure (1–1000 atm) range, as described in equation (3).  

$$\log_{10} K_p = \frac{2001.6}{T} - 2.69112 \log_{10} T - 5.519265 \times 10^{-5} T + \delta 1.848863 \times 10^{-7} T^2 + 2.6899$$  \hspace{1cm} (3)

Since then, this correlation has been widely applied to estimate the equilibrium constants for NH₃ synthesis (i.e. Gaine [17]; Elnashaie et al. [18]; Twigg [19]) and applied to indirectly calculate equilibrium constants for NH₃ cracking reactions in recent studies [20–22].

![Figure 2. Conversion levels of NH₃ under different operating conditions at chemical equilibrium](image)

The equilibrium constant ($K_p$) in equation (3), can be used to calculate levels of NH₃ conversion at chemical equilibrium under different temperatures and pressures. The results are plotted in figure 2. As shown in the figure, decomposition of NH₃ increases as the temperature rises, but decreases as pressure increases. The shaded area in figure 2 represents the operating conditions under which we intend to run our NH₃ decomposition reactor, which is the first stage of the H₂ generation process described in figure 1. According to chemical equilibrium calculation, NH₃ cracking of >95% can be achieved at 450–550 °C and 1–10 bar operating pressure. Therefore, it is reasonable to assume that NH₃ cracking conversions (80–90%) used in the following calculations are feasible.
3. Modelling of Membrane Reactor

3.1. Reactor configuration
An isometric diagram of the H₂ membrane reactor used in this study is presented in figure 3(a). The reactor consists of 19 tubular membrane tubes (each 470 mm long and 9.5 mm in diameter) inside a tubular shell with an inner diameter of 130 mm. A side view of the reactor presenting the arrangement of the membrane tubes inside the reactor is given in figure 3(b). The reactor geometry was constructed for a 3D model using the 3D-modelling software SpaceClaim. The mesh of the fluid volume inside the reactor was generated using ANSYS Meshing. A cross-section view and an isometric view of the resulting meshes consisting of 600,000 cells are shown in figure 4. As shown in figure 4, finer meshes were created in the near-wall region to achieve accurate local wall shear predictions.

![Figure 3(a). Isometric diagram of H₂ membrane reactor](image)

![Figure 3(b). Side view of the membrane reactor](image)

![Figure 4. Mesh at symmetry surface and back side of fluid volume inside the membrane reactor](image)

3.2. H₂ permeation submodel
H₂ permeation flux through the metal membrane can be expressed by:

\[
J_{H_2} = \frac{P_e}{\delta} \left( P_{H_2,ret}^n - P_{H_2,perm}^n \right)
\]  

(4)

where

\[ J_{H_2} = \text{the H}_2 \text{ diffusion flux through the metal membrane (mol m}^{-2} \text{s}^{-1}) \]
\[ \delta = \text{thickness of membrane (m)} \]
\[ P_{H_2} = H_2 \text{ partial pressure (Pa) in the retentate (ret) and permeate (perm) streams} \]
\[ P_e = \text{the } H_2 \text{ permeability (mol.m m}^{-2}\text{ s}^{-1}\text{ Pa}^{-0.5}) \]

The \( H_2 \) permeability \( (P_e) \) is the temperature-dependent parameter, which is usually defined by the Arrhenius equation. However, in this study, our focus was to investigate the performance of the membrane reactor under isothermal conditions at a constant operating temperature of 300 °C. Therefore, a constant \( H_2 \) permeability of \( 3.0E^{-07} \text{ mol.m m}^{-2}\text{ s}^{-1}\text{ Pa}^{-0.5} \) measured from our previous experimental work has been used for model simulations. The thickness of membrane used was 0.25 mm. In equation (4), \( n \) is the power dependency of the \( H_2 \) concentration on its partial pressure. The ‘\( n \)’ factor can have a value of between 0.5 and 1, and can be calculated from the correlation between \( H_2 \) pressure and permeation flux [23, 24]. In this study, the mass transport of \( H_2 \) is assumed to be controlled by diffusion of atomic hydrogen, so that the process can be described by the Sieverts-Fick law, and \( n \) factor is taken as 0.5.

3.3. Model formulation
The standard transport equations governing 3D modelling were derived from the laws of conservation of mass, momentum and energy. Details of these equations can be found in any heat and mass transfer texts and are also outlined in the ANSYS Fluent manual [25]. The governing equations were solved using commercial CFD software ANSYS Fluent 18.0. Gas flow and mixing were modelled using the two-equation standard k-epsilon model for closure. Coupled solver was used for pressure–velocity coupling, enabling a pseudo transient option with pseudo time steps of 0.01 s. The thermophysical and transport properties of gas species and gas mixtures are defined using submodels readily available in Fluent [25].

The calculations for \( H_2 \) permeation rates across the V-supported membrane tubes were separately developed in C++ programming language and exported to Fluent as a user-defined function. All of the governing equations considered in the pressure-based 3D model were then solved simultaneously using ANSYS Fluent version 18.0.

4. Model simulation results and discussion
The main objective of this study is to investigate the performance of membrane reactors focusing on \( H_2 \) yield and total \( H_2 \) generation under different \( NH_3 \) inlet flow rates and different \( NH_3 \) decomposition levels in the first stage of the system. The baseline input parameters to the 3D membrane reactor model are listed in table 1. As discussed Section 3, the assumption of \( NH_3 \) decomposition was justified by the chemical equilibrium calculation. The operation of the membrane reactor was assumed to be isothermal, which means inlet temperature of the gas mixture, membrane reactor temperature and outlet gas temperature are constant at the value listed in table 1. The inlet gas pressure was assumed to be 7.8 bar, which is 1 bar below the vapour pressure of \( NH_3 \) at 21 °C. As described in equation (4), \( H_2 \) separation through the membrane is driven by the \( H_2 \) partial pressure difference across the membrane. In order to maximise \( H_2 \) yield, a vacuum was applied to the permeate side of the membrane and the pressure was taken as 0.1 bar.
Table 1. Baseline operating parameter values used for model simulations

| Parameter                                      | Value            |
|-----------------------------------------------|------------------|
| NH$_3$ inlet to the system                    | 35 L min$^{-1}$  |
| NH$_3$ decomposition                          | 90 %             |
| H$_2$ inlet to membrane reactor              | 66.7 mol%        |
| N$_2$ inlet to membrane reactor              | 22.2 mol%        |
| NH$_3$ inlet to membrane reactor              | 11.1 mol%        |
| Operating temperature (isothermal)           | 300°C            |
| Total pressure of the gas mixture             | 7.8 bar$\text{a}$ |
| Pressure on permeate side of membrane         | 0.1 bar$\text{a}$ |

Gas velocity magnitudes with vectors are shown in figure 5(a), while figure 5(b) highlights the cross-sectional profiles of gas velocity contours at the outlet of the metal membranes. As more than half of the inlet gas flowed through much smaller spaces inside the membrane tubes, significantly higher velocities of H$_2$ were found inside the membrane tubes, especially in those located closer to the reactor’s centre. It is expected that the flow profile of the inlet gas mixture reached a maximum along the centreline of the reactor, which yielded higher H$_2$ separation rates and consequently higher H$_2$ flows inside the membrane tubes around the centreline.

Figure 5(a). Velocity magnitude with vectors

Figure 5(b). Velocity contour at H$_2$ outlets

The contours of the molar concentration of H$_2$ are shown in figure 6. Pure H$_2$ flows inside the membrane tubes, and a very low concentration of H$_2$ is present in the retentate stream at the outlet.
Figure 6. Contours of H$_2$ molar fraction

4.1. Effect of feed-gas flow rates

To enhance our understanding on the performance of the membrane reactor, a parametric analysis was carried out to explore the effects of variation in total feed-gas flow rate and level of NH$_3$ cracking efficiency on total H$_2$ production rates and H$_2$ yield. The results are shown in figure 7 and figure 8.

In this study, H$_2$ yield for the membrane reactor is defined as:

$$H_2 \text{ yield}\% = \frac{H_2 (\text{mol})_{\text{out (permeate)}}}{H_2 (\text{mol})_{\text{feed gas}}} \times 100$$ (5)

The shaded area in figure 7 represents the range of expected H$_2$ production (4.6–11.6 kg/day) for a range of NH$_3$ consumption rates (43–108 Nm$^3$/day) and NH$_3$ cracking efficiencies (80–90%), while the dotted lines represent the theoretical maximum possible H$_2$ production rate under the same operating conditions. The theoretical maximum H$_2$ production rate is defined as a condition where the H$_2$ pressure on feed side equalises with H$_2$ pressure on permeate side. As shown in figure 7, H$_2$ production rates at lower NH$_3$ inlet flow rates were found to be much closer to theoretical maximum values. For higher NH$_3$ inlet flow rates, the gaps between maximum possible H$_2$ production rates and estimated H$_2$ production rates of the membrane reactor became more significant. This phenomenon can be explained by figure 8, which shows the accumulated H$_2$ yield along the membrane tubes for different NH$_3$ flow rates. As expected, at lower NH$_3$ inlet flow rates, gas mixture velocities were slower and residence times were consequently longer. As a result, higher H$_2$ yields could be obtained within a shorter distance. Conversely, at high flow rates, H$_2$ yield is significantly lower due to shorter residence times. Even though relatively high H$_2$ yields were possible at the outlet of the membrane reactor under higher NH$_3$ inlet flow rates, the calculated H$_2$ yields were found to be lower than the theoretical maximum values.
Figure 7. \(\text{H}_2\) production rates calculated for different \(\text{NH}_3\) inlet flow rates

Figure 8. Accumulated \(\text{H}_2\) yield along membrane tubes for different \(\text{NH}_3\) inlet flow rates (90% \(\text{NH}_3\) cracking efficiency)

4.2. Effects of permeability

In this study, a constant \(\text{H}_2\) permeability value of 3.0E–07 mol·m·m⁻²·s⁻¹·Pa⁻⁰·⁵ was used for model simulations. This value was derived from experimental testing of the metal membranes at 300°C. A parametric analysis was carried out under selected operating conditions (\(\text{NH}_3\) inlet flow of 50.4 Nm³·h⁻¹ and 90% \(\text{NH}_3\) cracking efficiency) to explore the effects of changes in permeability of membrane tubes on membrane reactor performance. In the simulations, we varied the permeability to 50, 20 and 10% of the original set value (figure 9). The results show that similar level of high \(\text{H}_2\) yields could still be obtained at the \(\text{H}_2\) outlets even when the metal membranes functioned at only 50% of their empirical permeability. \(\text{H}_2\) yields were significantly reduced at lower levels of membrane permeabilities; for example, with metal membranes functioning only at 10% of base-case permeability, \(\text{H}_2\) yield was reduced to 52%.
5. Summary
A 3D CFD model has been developed to investigate the performance of a metal membrane reactor for H₂ production via NH₃ decomposition. Model simulation estimated that a range of H₂ production rates of 4.6–11.6 kg/day are possible for the range of operating conditions investigated. Model results showed that close to theoretical maximum H₂ yields could be achieved when the reactor was operated under lower inlet NH₃ flows. A parametric study was conducted to investigate the effects of membrane permeability on the H₂ yield. The results showed that a similar level of high H₂ yield could be still obtained at the H₂ outlets even if metal membranes functioned at only 50% of their original permeability.

The main objective of this study is to enhance our understanding of the H₂ separation process in H₂/N₂/NH₃ gas mixtures, and to design a H₂ membrane reactor with H₂ production rates of 5–10 kg/day from ammonia. Fabrication and assembly of this prototype plant are in progress. The next step of this study, therefore, will be to check the validity of CFD modelling results from this study by comparing with performance of the H₂ production reactor via ammonia using an experimental system which will be available for operation in near future.

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