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Numerical Analysis of the Performance of Membrane Reactors for NH_3 Decomposition

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An analysis of the performance of a membrane reactor for the production of pure hydrogen through ammonia decomposition is presented here. The system is numerically studied under a wide range of operating conditions to identify those most favorable for the production of pure hydrogen. The underlying idea is that, in the case of ammonia decomposition, a membrane reactor allows to operate at low temperature not only because the selective removal of hydrogen shifts the equilibrium of the reactor towards the products, but also because the reaction rate is enhanced by the removal of hydrogen, which at low temperatures inhibits the kinetics of ammonia decomposition.

1. Introduction

The use of hydrogen as a clean energy vector has been attracting increasing interest. Hydrogen for fuel cell applications, however, requires extremely high degrees of purity. In addition, problems related to its transport and storage have led to the need of developing compact systems that allow its distributed production and use. In this view, membrane reactors for the production of hydrogen are being extensively studied. These systems have been proposed mainly for steam reforming of different hydrocarbon fuels including methane (Kyriakides et al., 2016, Dittmar et al., 2013), methanol (Israni and Harold, 2010), and biogas (Vasquez-Castillo et al., 2015). All these reactions are strongly endothermic, but the use of membrane reactors allows to lower the operating temperatures compared to those required in traditional processes because the selective removal of hydrogen while it is being produced shifts the reaction equilibrium toward higher feed conversions. Lowering the operating temperature represents an advantage not only in terms of the energetic requirements of the process, but also allows the use of more compact heating systems compared to furnaces.

In the recent years there has been increasing interest in the use of membrane reactors for ammonia decomposition. In this scenario, ammonia would be used as a hydrogen carrier, thereby avoiding the problems related to the transport and storage of hydrogen in off-board hydrogen production systems. Compared to the steam reforming of hydrocarbons, the ammonia decomposition reaction is characterized by an almost complete conversion at equilibrium already at temperatures of approximately 400°C; however, problems arise when taking into consideration the reaction rate. Studies have shown that at low temperatures the rate of hydrogen production in inhibited by the presence of hydrogen itself (Djega-Mariadassou, 1999). The use of membrane reactors could therefore allow to overcome both thermodynamic and kinetic limitations of ammonia decomposition. The present work is divided as follows. In Section 2, an overview is presented of the kinetics of ammonia decomposition and its consequence on the proposal of utilizing a membrane reactor. In Section 3, the model employed is discussed, in both its dimensional and dimensionless form. The results are discussed in Section 4.

2. Ammonia decomposition kinetics

The heterogeneous catalytic decomposition of ammonia

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad \Delta H = 91.8\ \text{kJ/mol} \qquad (1)$$

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over metal-based catalysts takes place according to the following reaction sequence: ammonia adsorption (2a), surface reactions (2b-2d), nitrogen desorption (2e) and hydrogen desorption (2f).

$$2NH_3 + 2a \rightarrow 2(NH_3)_a \tag{2a}$$

$$2(NH_3)_a + 2a \rightarrow 2(NH_2)_a + 2(H)_a \tag{2b}$$

$$2(NH_2)_a + 2a \rightarrow 2(NH)_a + 2(H)_a \tag{2c}$$

$$2(NH)_a + 2a \rightarrow 2(N)_a + 2(H)_a \tag{2d}$$

$$2(N)_a \rightarrow N_2 + 2a \tag{2e}$$

$$6(H)_a \rightarrow 3H_2 + 6a \tag{2f}$$

where *a* indicates the adsorption sites.

Ammonia adsorption (2a), surface reaction (2b), and ammonia desorption (2e) have been identified as possible rate-determining steps, depending on the active catalyst component; however, even for the same metal, differences in reaction rate were measured for different crystallographic planes, as discussed in (Mukherjee et al., 2018), and an effect of operating temperature on the rate-determining step was found on catalysts of the same kind (Lanzani and Laasonen, 2010).

The first studies on the kinetics of ammonia decomposition were carried out at low ammonia partial pressures (Oyama, 1992), which was achieved either by using pure ammonia at low pressures or a diluted feed at higher pressures. As outlined in (Chellappa et al., 2002), two main conclusions were reached from these studies

1. At temperatures lower than 500°C and high hydrogen partial pressures, the reaction rate is inhibited by hydrogen and can be described by the Temkin-Pyzhev model

   $$r = k\left(\frac{p_{NH_3}^2}{p_{H_2}^3}\right)^{\beta} \tag{3}$$

   with β ranging between 0.25 and 0.60, whereas at higher temperatures and low hydrogen partial pressures, the reaction rate is only dependent on the partial pressure of ammonia. The model describing such behavior in known as the Tamaru model

   $$r = kp_{NH_3}^{\alpha} \tag{4}$$

2. At low pressures and low ammonia partial pressures, the reaction is zero-order with respect to ammonia. An increase in temperature at low ammonia partial pressure leads to the reaction rate becoming first-order with respect to ammonia

More recent studies have focused on the kinetics of ammonia decomposition for higher ammonia partial pressures. Similarly to the previous studies, it was found that at high temperatures, approximately above 500°C, the reaction rate was only dependent on the partial pressure of ammonia (Chellappa et al., 2002), whereas at lower temperatures an inhibiting effect of hydrogen becomes significant (Zhang et al., 200).

In light of these observations, it can be concluded that the use of a membrane reactor for the production of hydrogen through the decomposition of ammonia at low temperatures, i.e., <500°C would have the two-fold advantage of shifting the equilibrium toward the products through the selective removal of hydrogen as well as favoring the reaction kinetics by removing the inhibiting component. The present work aims at an analysis of the behavior of an ammonia decomposition membrane reactor and the identification of the most favorable operating conditions. The rate of ammonia decomposition was described through a Temkin-Pyzhev-type expression. The rate expression was modified to account for the distance from equilibrium, obtaining an analogous reaction rate expression to that proposed by Lamb et al. (Lamb et al., 2019) to describe the rate of the reaction on a LiOH-promoted, αAl_2O_3-supported Ru catalyst. This modification becomes necessary when modeling membrane reactors, because selectively removing hydrogen simultaneously to its production may lead to the reactor operating in near-equilibrium conditions. The reaction rate expression used is therefore

$$r = k\left(\frac{p_{NH_3}^2}{p_{H_2}^3}\right)^{\beta}(1-\eta) \tag{5}$$

with β=0.25 and where

$$\eta = \frac{1}{K_{eq}}\frac{\left(p_{H_2}\right)^3 p_{N_2}}{\left(p_{NH_3}\right)^2} \tag{6}$$

3. Model formulation

The system considered consists of a tube-in-tube reactor. The reaction takes place in the annular volume between the two tubes, where the catalyst is placed. The radii of the outer and inner tubes are denoted as R_2 and R_1, respectively; the length of the reactor is indicated as L. The hydrogen-permeable membrane is placed on the outer wall of the innermost tube. The cylindrical volume inside the innnermost tube is the permeate side. The model was developed under the following assumptions

1. Constant and uniform temperature - previous studies on steam reforming membrane reactors showed that it is possible to achieve a uniform temperature profile (Said et al. 2016). The significantly lower heat of reaction of ammonia decomposition compared to methane steam reforming, 90 vs. 180 kJ/mol, means that such a conclusion may be easily extend to the reaction system considered in the present work.
2. Zero hydrogen partial pressure in the permeate side. This may be achieved either by creating vacuum conditions in the permeate or by using a high sweep gas flow rate to remove hydrogen produced in the retentate side and that permeated across the membrane.
3. Infinite membrane selectivity toward hydrogen. This assumption is verified whenever using dense Pd-based membranes, which have been experimentally shown such behavior.
4. Negligible membrane permeance inhibition by ammonia and nitrogen, justified by previous findings (Murmura and Sheintuch, 2018).

The 2D model accounts for mass and momentum transport in the radial and axial directions, more specifically

- The velocity profile of the gas in the packed bed has been evaluated through Darcy's law for flow in porous media

$$\mathbf{v} = \frac{\mathbf{1}}{U}\frac{\kappa}{\mu}\frac{P_{atm}}{R_1}\nabla P \tag{7}$$

- Based on Eq.(7), the continuity equation in conditions of constant temperature

$$\boldsymbol{\nabla}\cdot(\rho\mathbf{v}) = \mathbf{0} \tag{8}$$

becomes

$$\boldsymbol{\nabla}\cdot(\rho\nabla P) = \mathbf{0} \tag{9}$$

- The effect of changes in total pressure and gas composition on the density of the gas mixture have been taken into consideration, assuming an ideal behavior of the gas; therefore, Eq.(9) becomes

$$\boldsymbol{\nabla}\cdot(fP\nabla P) = \mathbf{0} \tag{10}$$

having expressed the density as

$$\rho = \frac{fP}{RT} \tag{11}$$

where f is the average molecular weight of the mixture

$$\frac{1}{f} = \frac{\omega_a}{W_a} + \frac{\omega_h}{W_h} + \frac{1-\omega_h-\omega_a}{W_n} \tag{12}$$

where the symbols ω_i and W_i have been used to identify the mass fraction and molecular weight of the i-th component, and the subscripts a, h, and n refer to ammonia, hydrogen, and nitrogen, respectively.

- Both axial and radial components of velocity are considered.
- Mass transport by convection and dispersion in both the radial and axial directions is accounted for.
- The rate of ammonia decomposition is described through a Temkin-Pyzhev model including a term accounting for the distance from equilibrium, as described in Eq.(5).
- Hydrogen permeation across the membrane has been described through Sieverts' law, valid for dense membranes (Ward and Dao, 1999)

$$J_{H_2} = \mathbb{P}_m \left(\sqrt{p^r_{H_2}} - \sqrt{p^p_{H_2}} \right) \tag{13}$$

where J_{H2} is the hydrogen mass flux, $\mathbb{P}_m$ is the membrane permeability, whose value depends on the membrane material, thickness, and on the operating temperature, and p^r_{H2} and p^p_{H2} are the partial pressures of hydrogen in the retentate and permeate sides, respectively. When introducing the simplifying assumption discussed above of zero hydrogen pressure in the permeate side, Eq.(13) above becomes

$$J_{H_2} = \mathbb{P}_m \sqrt{p^r_{H_2}} \tag{14}$$

The mass balance equation for the i-th component is therefore

$$\frac{1}{RT} \nabla \cdot \left(-\frac{\kappa}{\mu} fP\omega_i \nabla P - fP\mathbb{D} \cdot \nabla\omega_i \right) = r_i \tag{15}$$

Where $\mathbb{D} = \begin{pmatrix} \mathcal{D}_{rr} & 0 \\ 0 & \mathcal{D}_{rzz} \end{pmatrix}$ is a non-isotropic effective dispersion tensor, and where r_i denotes the rate of production of the i-th component by the chemical reaction per unit volume and unit time.

The boundary conditions for the momentum and mass balance equations are as follows:

- at the inlet cross-section of the annular region, $z=0$, $R_1 \le r \le R_2$ we assume uniform velocity of the gas, U
- the composition of the feed stream is considered to be pure ammonia, with traces of hydrogen, $\omega_h = 0.01$. This corresponds to considering the feed to the reactor as the product of a stream deriving from a Haber process with roughly 99% hydrogen conversion and neglecting the low residual nitrogen concentration.
- at the outlet cross-section, $z=L$, $R_1 \le r \le R_2$ a uniform and fixed pressure, P_L is assumed
- purely convective flux is assumed for all the species at the outlet of the reactor

  $$\left.\frac{\partial\omega_i}{\partial z}\right|_{z=L} = 0 \tag{16}$$

- impermeability to all components is set on the outer wall

  $$\nabla \mathrm{P} \cdot \mathbf{n}|_{r=R_2} = 0 \tag{17}$$

  $$\nabla\omega_i \cdot \mathbf{n}|_{r=R_2} = 0 \tag{18}$$

  where **n** is the local unit vector normal to the surface and oriented outward the reaction volume
- impermeability to all components except hydrogen is imposed on the inner wall, leading to the following conditions for hydrogen

  $$\left.\left(-\frac{\kappa}{\mu} fP\omega_h \nabla P - fP\mathbb{D} \cdot \nabla\omega_h \right) \cdot \mathbf{n} \right|_{r=R_1} = RT\mathbb{P}_m \sqrt{\omega_h fP/W_h} \tag{19}$$

  all other components ($i \neq h$)

  $$\left.\left(-\frac{\kappa}{\mu} fP\omega_i \nabla P - fP\mathbb{D} \cdot \nabla\omega_i \right) \cdot \mathbf{n} \right|_{r=R_1} = 0 \tag{20}$$

  and total flux

  $$\left.\left(-\frac{\kappa}{\mu} fP\nabla P \right) \cdot \mathbf{n} \right|_{r=R_1} = RT\mathbb{P}_m \sqrt{\omega_h fP/W_h} \tag{21}$$

The model was solved using the finite-element solver COMSOL Multiphysics. The mesh used to solve the problem consisted of elements of smaller size near the membrane wall, where higher concentration gradients are observed, and larger elements near the impermeable wall. The computational time required to solve the problem was about 10 minutes in an i7, 16 GB RAM computer.

4. Overview of main results

The behavior of membrane reactors for ammonia decomposition has been numerically studied through CFD simulations over a wide range of operating conditions. The operating parameters that have been varied in the course of the analysis are the operating pressure, membrane permeability, inlet gas velocity, mass diffusivity, and kinetic constant. Typical operating conditions are reported in Table 1. The performance of the system has been studied in terms of the dimensionless permeate flow rate, Π_h, defined as the ratio between the hydrogen permeate and inlet flow rates.

Table 1: Typical operating conditions in membrane reactors for ammonia decomposition

Parameter	Value
R_1 [m]	0.1
R_2 [m]	0.25
L [m]	0.5
U [m/s]	0.5
$\mathbb{P}_m$ [$kg_{H2}/sm^2Pa^{0.5}$]	2.5×10^{-5}
k [$kg_{H2}Pa/m^3s$]	50
$\mathcal{D}$ [m^2/s]	3×10^{-3}

In past works carried out by some of the same authors regarding the behavior of membrane reactors for methane steam reforming it was noticed that as the operating pressure is increased, while maintaining the inlet gas velocity and all other operating conditions constant, the behavior of the reactor went from being limited by hydrogen transport within the packed bed to be hydrogen across the membrane (Murmura et al. 2017). This change in limiting mechanism was evidenced by a variation in the slope of the curve of hydrogen permeate flow rate vs. pressure, which switched from 1 in the mass transport-controlled regime to 0.5 in the membrane permeation-controlled regime. The pressure value at which such a change occurred is a function of the mass dispersion coefficient in the packed bed and the membrane permeability. A similar observation can be made in the case of the membrane reactor for ammonia decomposition, as shown in Figure 1, where it can be seen that that, under the operating conditions described in Table 1, at a pressure of approximately 3 atm, the slope of the curve of the permeate flow rate vs. pressure decreases rapidly. Such a change in the slope of the curve identifies the pressure value for which the mechanism limiting the rate of hydrogen permeation goes from being hydrogen transport within the packed bed to hydrogen permeation across the membrane. This result highlights the fact that the presence of the selectively permeable membrane enhances the reaction kinetics through the removal of hydrogen – the inhibiting component – to the point that the rate of reaction is no longer the factor limiting the behavior of the system.

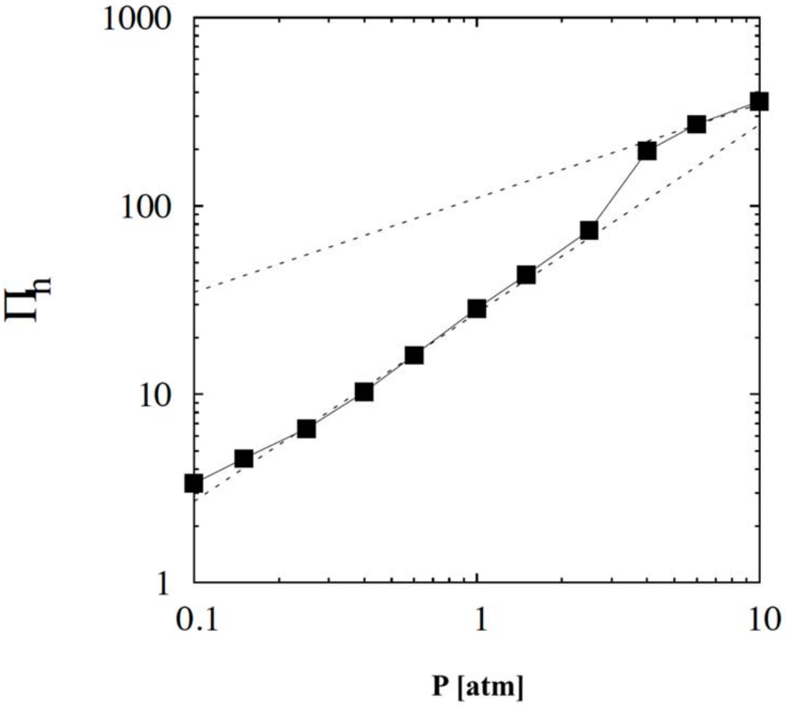

Figure 1: Dimensionless permeate flow rate vs. pressure for an ammonia decomposition reactor under the operating conditions summarized in Table 1

5. Conclusions

This work presents a preliminary numerical analysis of membrane reactors for ammonia decomposition in which a hydrogen permeable membrane is employed to enhance the performance of the system. Membrane reactors are most commonly employed to shift the equilibrium conditions. In the case of ammonia decomposition, approximately a 99% conversion at equilibrium can be attained already at temperatures around 400°C; on the other hand, the produced hydrogen inhibits the reaction, thereby lowering its rate. The use of hydrogen permeable membrane is therefore important to enhance the process kinetics and decrease the reactor dimensions.

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