Heat Transfer Modelling of Steam Methane Reforming

Elena Carcadea*, Mihai Varlam, Ioan Stefanescu

National Research Institute for Isotopic & Cryogenic Technologies, Rm.Valcea, Romania
Street Uzinei no.4; O.P Râureni; P.O.Box 7, Rm.Vâlcea, Code 240050, Romania,
elena.carcadea@icsi.ro

Abstract: The heat transfer modeling of a membrane reactor for methane steam reforming is investigated in this paper using COMSOL Multiphysics software.
In our simulation two domains were taken into account (reforming and permeating areas) while the membrane was considered one dimensional.
The temperature difference between the reforming and the sweep gas area was taken into account for giving us an insight regarding the interaction between the flow, chemical reaction and temperature.
The aim was to determine the maximum value of temperature in the sweep area of the porous membrane reactor, close to the inner permeation tubes, because the maximum values of temperature for long life and maximum performance of these tubes is close to 450K.

Keywords: methane reforming, modeling, heat transfer.

1. Introduction

The steam methane reforming process is the most widespread method for the hydrogen production. Many Research and Development programs are investigating the development of steam methane reforming technologies to enable the transition to sustainable energy, because it is considered that hydrogen can play a key role as an energy carrier.

Despite its importance, the conventional steam methane reforming process, carried out in fixed bed reactors has some disadvantages that can be overcome by using membrane reactors. The palladium membrane reactors have been identified as a promising option because it is possible to obtain a higher conversion than in traditional systems at the same operative conditions or to obtain the same conversions but at milder operating conditions. The use of a membrane reactor, where membrane are exclusively permeable to hydrogen and therefore pure hydrogen moves to the permeate side enabling the reactions to proceed towards completion, permits to reduce the number of steps for pure hydrogen productions.

Different experimental studies and theoretical modeling results have been reported in the literature trying to define the best suitable solution for a small-scale steam methane reforming membrane reactor [1-4].

2. Mathematical Model

A mathematical model for a membrane reactor is based on theoretical equations that describe the transport phenomena of the mass, momentum, energy and chemical species, and the process of selective permeation through membrane.

2.1 Kinetic Parameters

The main chemical reactions involved in the steam methane reforming process are:

\[
\begin{align*}
CH_4 + H_2O & \leftrightarrow 3 H_2 + CO \\
CO + H_2O & \leftrightarrow H_2 + CO_2 \\
CH_4 + 2 H_2O & \leftrightarrow 4 H_2 + CO_2
\end{align*}
\]

Several other reactions may occur in this process, but these reactions were not taken into consideration in our study.

It should be emphasized that CO₂ is not only produced via the shift reaction (2), but also directly via the methanation reaction (3). This implies that reaction (3) is not just the 'overall reaction', despite the fact that in literature steam-methane reforming is often considered to be a combination of reactions (1) and (2) only.

A number of kinetic rate expressions have appeared in the literature to describe the steam reforming of methane. These rate expressions vary from empirical expressions to ones based on fundamentals. In our work, the kinetic parameters are taken from work of Xu and Froment [1] where steam reforming of methane in a tubular reactor without membrane has been analyzed. The kinetic rates of adsorption or production of the gas species, based on partial
pressure, temperature and species compositions for the chemical reactions are given by [5]:

\[
R_1 = \frac{k_1}{P_{H_2}^{2.5} \cdot \text{DEN}^2} \left[ P_{CH_4}P_{H_2O} - \frac{P_{H_2}P_{CO}}{K_{e1}} \right]
\]

(4)

\[
R_2 = \frac{k_2}{P_{H_2} \cdot \text{DEN}^2} \left[ P_{CO}P_{H_2O} - \frac{P_{H_2}P_{CO_2}}{K_{e2}} \right]
\]

(5)

\[
R_3 = \frac{k_3}{P_{H_2}^{1.5} \cdot \text{DEN}^2} \left[ P_{CH_4}P_{H_2O} - \frac{P_{H_2}P_{CO_2}}{K_{e3}} \right]
\]

(6)

\[
\text{DEN} = 1 + K_{CH_4}P_{CH_4} + K_{CO}P_{CO} + K_{H_2}P_{H_2} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}}
\]

(7)

The kinetic rate constants, \(k_i\), the adsorption constants, \(K_j\) and the equilibrium constants, \(K_{ej}\), are given by the Arrhenius type relationships as follows [6]:

\[
k_1 = 4.22 \times 10^{15} \exp(-240100/RT)
\]

(8)

\[
k_2 = 1.96 \times 10^6 \exp(-67130/RT)
\]

(9)

\[
k_3 = 1.02 \times 10^{15} \exp(-243900/RT)
\]

(10)

\[
K_{CH_4} = 6.65 \times 10^{-4} \exp(38280/RT)
\]

(11)

\[
K_{H_2O} = 1.77 \times 10^5 \exp(-88680/RT)
\]

(12)

\[
K_{H_2} = 6.12 \times 10^{-9} \exp(82900/RT)
\]

(13)

\[
K_{CO} = 8.23 \times 10^{-5} \exp(70650/RT)
\]

(14)

\[
K_{e1} = 5.75 \times 10^{12} \exp(-11476/RT)
\]

(15)

\[
K_{e2} = 1.26 \times 10^{12} \exp(4639/RT)
\]

(16)

\[
K_{e3} = 7.24 \times 10^{10} \exp(-21646/RT)
\]

(17)

2.2 Governing equations

The mathematical model of a reactor is based on theoretical equations that describe the transport phenomena of the mass, momentum, energy, chemical species, and the process of selective permeation through membrane.

The reactor is modeled taking into account those two sub-domains: the feed side and the permeation side, separated by the membrane, as can be seen in figure 1. The model couples equations for mass, momentum, energy and chemical species to describe the conditions within the reactor.

The pressure loss in the feed side is modeled by Darcy law. Diffusive mass transfer takes place in the r direction, and is introduced by the Stefan-Maxwell diffusion equations. \(H_2\) permeation across the membrane is described by Sievert’s law.

Partial pressures of gases were correlated to their own concentrations by using the ideal gas law.

In the species mass conservation equations, the source terms \(S_i\) giving the rate of production or depletion of the species \(i\) are:

\[
S_{H_2} = (3R_1 + R_2 + 4R_3) \cdot M_{H_2}
\]

(18)

\[
S_{CH_4} = (-R_1 - R_3) \cdot M_{CH_4}
\]

(19)

\[
S_{H_2O} = (-R_1 - R_3 - 2R_3) \cdot M_{H_2O}
\]

(20)

\[
S_{CO} = (R_1 - R_2) \cdot M_{CO}
\]

(21)

The mass fraction of the last component is determined by subtracting the sum of the mass fractions of all the other components from unity.

In the permeation side laminar flow is applied. No reaction takes place on the permeate side. Mass transport across the membrane is modeled using Sievert’s law. The rate of \(H_2\) permeation per unit area of the membrane, \(J_{H_2}\) (mol/m²·s), is proportional to the partial pressure difference according to the equation [22]:

\[
J_{H_2} = \frac{A_0 \exp(-E_{a}/RT)}{\delta} \left( p_{H_2}^{0.5} - p_{H_2}^{0.5} \right)
\]

(22)
where the $A_0$ is the pre-exponential factor of the hydrogen permeability, $E_a$ is the activation energy and $\delta$ is the membrane thickness $(A_0 = 1.7 \times 10^{-10} \text{mol/m}^2\text{sPa}^{-0.5}, E_a = 6170 \text{J/mol})$.

The energy balance for describing the average temperature distribution is:

$$\rho \ C_p \ \overrightarrow{u} \ \nabla T + \nabla \cdot (-k \ \nabla T) = S_T$$

where $C_p$ is the fluid heat capacity at constant pressure and $k$ is thermal conductivity. The heat source term $S_T$ (W/m$^3$) is zero in the permeation area and it is associated with the steam reforming, water gas-shift and methanation reactions:

$$S_T = \rho_{\text{mix}} \sum_i \left( -\Delta H_{f_i} / r_i \right)$$

where $\Delta H_{f_i}$ is the enthalpy of reaction $i$ and $r_i$ is the rate of reaction $i$ (mol/m$^3$ s), $i = 1, 2, 3$.

The heat exchange between the reformer area and the permeation zone, described by [9]:

$$q = \begin{cases} -h_t (T - T_p) & \text{in the reformer area} \\ h_t (T - T_p) & \text{in the permeating area} \end{cases}$$

Due to the strongly endothermic nature of the process, a big amount of heat has to be supplied in order to fulfill the energy adsorbed by reactions. The inward heat flux through the external wall is given by: $q = h_{\text{wall}} (T_{\text{ext}} - T_r)$, where $h_t$ and $h_{\text{wall}}$ are the heat transfer coefficients (W/(m$^2$K)) between the reformer and permeation area, respectively between the surroundings (external zone) and the reactor wall.

2.2 Boundary conditions

In the permeation side an inlet velocity is given for the momentum transport (0.8m/s). In the feed side a pressure drop of 75 Pa was given for the momentum transport equation. Influence of hydrogen transport across the membrane on the velocity is accounted for using source terms. The transport across other boundaries is constrained to zero.

Regarding the species conservation a composition for the mixture is given in mass fraction terms. Usually, methane (CH$_4$) and water (H$_2$O) are fed as reactants in the reactor, and carbon dioxide (CO$_2$), carbon monoxide (CO), and hydrogen (H$_2$) are produced over a catalyst but from convergence reasons a small quantity of H$_2$, CO and CO$_2$ was introduced in the feed stream. The mixture composition at the feed side inlet is CH$_4$:H$_2$O:H$_2$:CO$_2$:CO-0.23:0.75:0.018:0.001:0.001 and for the permeate side the sweep gas mass fraction is 1.

For the energy conservation, in both areas a constant temperature was prescribed for the inlet. Also, on the external wall of the reactor a constant temperature has been set up. Also, on the membrane and on the external wall a heat flux was defined.

At the outlet, convective flux conditions are specified for all species. Excepting H$_2$, all other species cannot penetrate through walls, since insulation conditions are chosen.

3. Results and Discussions

The membrane reactor geometry was built in COMSOL Multiphysics software as a 2D-axisymmetric model, figure 1 [7]. The reactor configuration is quite simple and consists of an external tube with a serpentine shape for the reforming area and an inner tube for the sweep gas.

In our simulation the membrane was considered as a one dimensional domain, the boundary between the feed and permeation zone. It can be noticed that near the membrane where the flux of hydrogen takes place the triangular mesh is extremely fine. The parameters of fluid and porous media were taken from literature and are summarized in table 1.

<p>| Table 1: Parameters of Fluid and Porous Media |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of reactor</td>
<td>600</td>
<td>mm</td>
</tr>
<tr>
<td>Viscosity of feed side</td>
<td>2.7*10^{-5}</td>
<td>Pa·s</td>
</tr>
<tr>
<td>Permeability of feed side</td>
<td>2*10^{-10}</td>
<td>m$^2$</td>
</tr>
<tr>
<td>Porosity of feed side</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Inlet temperature of feed side</td>
<td>420/520</td>
<td>K</td>
</tr>
<tr>
<td>Viscosity of permeate side</td>
<td>10^{-4}</td>
<td>Pa·s</td>
</tr>
<tr>
<td>Inlet temperature of permeate side</td>
<td>300</td>
<td>K</td>
</tr>
<tr>
<td>Heat transfer coefficient between reformer and sweep area</td>
<td>100</td>
<td>W/m²K</td>
</tr>
<tr>
<td>Heat transfer coefficient between external area and reformer</td>
<td>500</td>
<td>W/m²K</td>
</tr>
</tbody>
</table>

COMSOL Multiphysics software was applied to analyze the steam methane reforming in the chemical reactor investigated. The model couples the Maxwell - Stefan Diffusion and Convection to the Darcy law and to Navier Stokes equation.

Excerpt from the Proceedings of the 2012 COMSOL Conference in Milan.
for both reforming and permeation zone, to account for the variation in gas density which results from the extraction/permeation of $H_2$.

The temperature difference between the reforming and the sweep gas area was analyzed in our study to give us an insight regarding the interaction between the flow, chemical reaction and temperature. The aim was to determine the maximum value of temperature in the sweep area of the porous membrane reactor, close to the inner permeation tubes, because the maximum values of temperature for long life and maximum performance of these tubes is close to 450°K.

In our simulation we have used two different values for the inlet temperature of the reforming area (420°K, 520°K) and we have varied the temperature of the external wall of the reactor in the range (573°K-1173°K).

The simulation results presented in figure 2 are obtained for 520°K inlet temperature in the reforming area and 573°K on the external wall of the reactor. It can be noticed that in the sweep (permeation) area an increase of temperature up to 398°K, which is a proper temperature for maximum performance and long life of permeation tubes.

It was found that an increase in the wall temperature of the reforming side has a positive effect in hydrogen production and permeation. In figure 3 a plot of maximum temperature of the permeation zone for two inlet temperature of the reforming zone (420°K, 520°K) can be seen. It can be noticed that the results are different, for 520°K inlet temperature in the reforming area and as the wall temperature increases the heat transfer between those two zones it decreases (the temperature is decreases) while for the 420 K inlet temperature in the reforming area and as the wall temperature increases the temperature is increasing. This occurs because the higher temperature in the reforming area promotes the steam methane reforming mechanism that consumes heat so that is why the temperature decreases for 520°K inlet temperature in the reforming area case.

Figure 2. Temperature in the Reforming area (left) and in the Permeation area of the reactor (right)

4. Conclusions

COMSOL Multiphysics software was applied to analyze the steam methane reforming in a chemical reactor. Our study was intended to give us an insight regarding the interaction between the flow, chemical reaction and heat transfer inside a porous membrane reactor.

Simulations are performed for different values of the external wall temperature and for two values of the reforming area inlet temperature. The aim was to determine the maximum value of temperature in the sweep area of the porous membrane reactor, close to the inner permeation tubes.

The simulation results showed that in the sweep area the temperature was up to 450°K while on the reforming side of the membrane the temperature was close to 617° K.

The main purpose of this study was to give us a better knowledge of the reactions involved in steam methane reforming process and an overview of the temperature influence on the reactor performance. An analysis of the effect of other parameters that has not been taking into consideration in this work and a model validation will be the subject for future research.

Figure 3. Maximum temperature in the permeation zone for two inlet temperature in the reforming zone (420°K, 520°K)
5. References