Heat Transfer Modelling of Steam Methane Reforming

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Introduction: The heat transfer modeling of a membrane reactor for methane steam reforming is investigated using COMSOL Multiphysics software.
The aim was to determine the maximum value of temperature in the sweep area, 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.

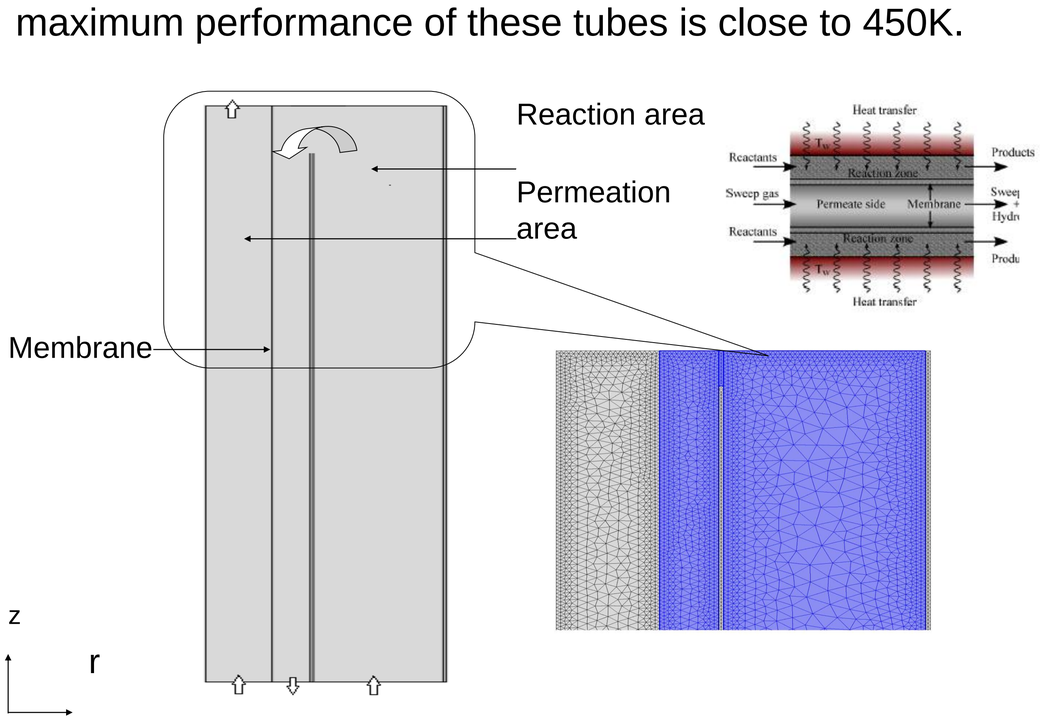


Figure 1. Membrane Reactor geometry (left) and a zoomed image of a mesh (right)

Model Development

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

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO$$
$$CO + H_2O \leftrightarrow H_2 + CO_2$$
$$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2$$

The mathematical model couples the equations for mass, momentum, energy and chemical species to describe the conditions within the reactor. The ideal gas behavior was assumed.
The flow of gaseous species through the reformer bed is described by Darcy's Law. The inlet and outlet boundary conditions describe a 75 Pa pressure drop across the feed side.
Diffusive mass transfer takes place along the reactor length and is introduced by the Stefan-Maxwell diffusion equations at steady state. In the species mass conservation equations, the rate of production or depletion of the species i are given by:

$$\begin{cases} S_{H_2} = (3R_1 + R_2 + 4R_3)\cdot M_{H_2} \\ S_{CH_4} = (-R_1 - R_3)\cdot M_{CH_4} \\ S_{H_2O} = (-R_1 - R_2 - 2R_3)\cdot M_{H_2O} \\ S_{CO} = (R_1 - R_2)\cdot M_{CO} \end{cases}$$

$$R_1 = \frac{\frac{k_1}{P_{H2}^{2.5}}\left[P_{CH4}P_{H2O} - \frac{P_{H2}^3 P_{CO}}{K_1}\right]}{DEN^2}\cdot m_{cat}$$

$$R_2 = \frac{\frac{k_2}{P_{H2}}\left[P_{CO}P_{H2O} - \frac{P_{H2}P_{CO2}}{K_2}\right]}{DEN^2}\cdot m_{cat}$$

$$R_3 = \frac{\frac{k_3}{P_{H2}^{3.5}}\left[P_{CH4}P_{H2O}^2 - \frac{P_{H2}^4 P_{CO2}}{K_3}\right]}{DEN^2}\cdot m_{cat}$$

$$DEN = 1 + K_{CH4}P_{CH4} + K_{CO}P_{CO} + K_{H2}P_{H2} + \frac{K_{H2O}P_{H2O}}{P_{H2}}$$

$[R_1, R_2, R_3]$= kmol/(kg_{cat}h)

k_i are the kinetic rate constants (kmol/(kg_{cat}h))

$$k_1 = 4.22\times10^{15}\exp(-240100/RT)$$
$$k_2 = 1.96\times10^{6}\exp(-67130/RT)$$
$$k_3 = 1.02\times10^{15}\exp(-243900/RT)$$

K_j are the adsorption constants

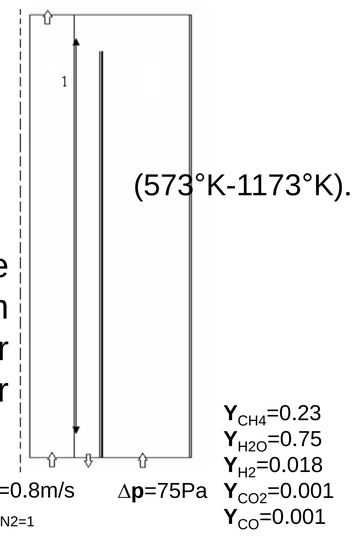
$$K_{CH4} = 6.65\times10^{-4}\exp(38280/RT), \text{ bar}^{-1}$$
$$K_{H2O} = 1.77\times10^{5}\exp(-88680/RT)$$
$$K_{H2} = 6.12\times10^{-9}\exp(82900/RT), \text{ bar}^{-1}$$
$$K_{CO} = 8.23\times10^{-5}\exp(70650/RT), \text{ bar}^{-1}$$

K_{ej} are equilibrium constants

$$K_{e1} = 5.75\text{x}10^{12}\exp(-11476/RT), \text{ bar}^2$$
$$K_{e2} = 1.26\text{x}10^{-2}\exp(4639/RT)$$
$$K_{e3} = 7.24\text{x}10^{10}\exp(-21646/RT), \text{ bar}^2$$

Numerical Results:

The membrane reactor geometry was built as a 2D-axisymetric model with the membrane considered as one dimensional (the boundary between the feed and permeation zone - 1).
The temperature difference between the reforming and the sweep gas area was analyzed to determine the maximum value of temperature in the sweep area, close to the inner permeation tubes. The maximum value of temperature for long life/max performance of these tubes is close to 450°K.



Parameter	Value	Unit
Length of reactor	600	mm
Viscosity of feed side	$2.7*10^{-5}$	Pa*s
Permeability of feed side	$2*10^{-10}$	m^2
Porosity of feed side	0.5	-
Inlet temperature of feed side	420/520	K
Viscosity of permeate side	10^{-4}	Pa*s
Inlet temperature of permeate side	300	K
Reformer/sweep area heat transfer coefficient	100	W/m^2K
External area/reformer heat transfer coefficient	500	W/m^2K

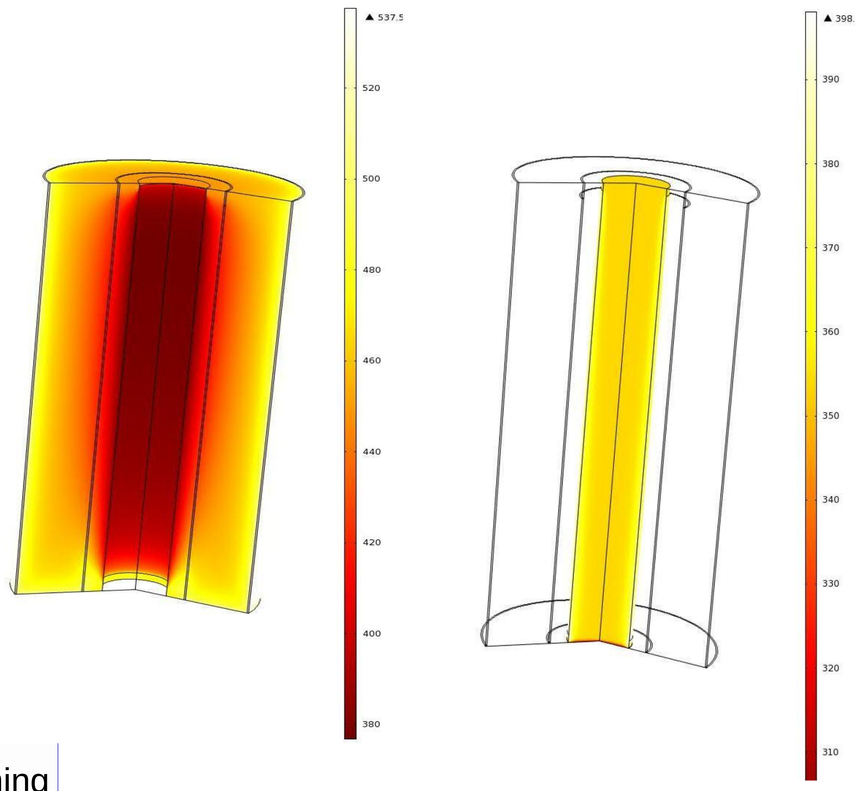


Figure 2. Temperature in the Reforming area (left) and in the Permeation area of the reactor (right)

2 values for inlet temperature of the reforming area : 420 K-520°K
and
a wall temperature in the range 573°K-1173°K
were tested

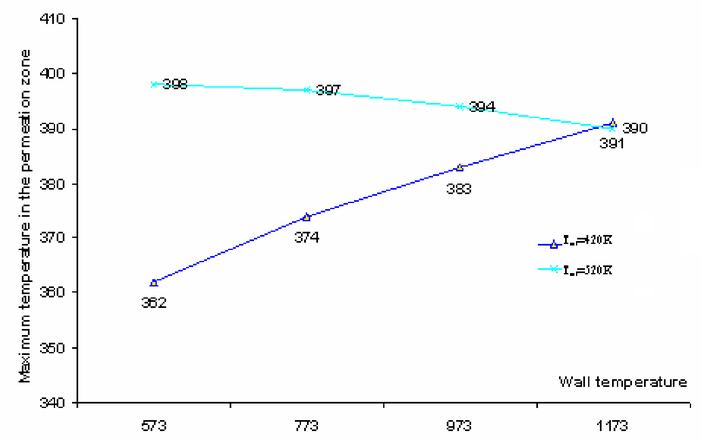
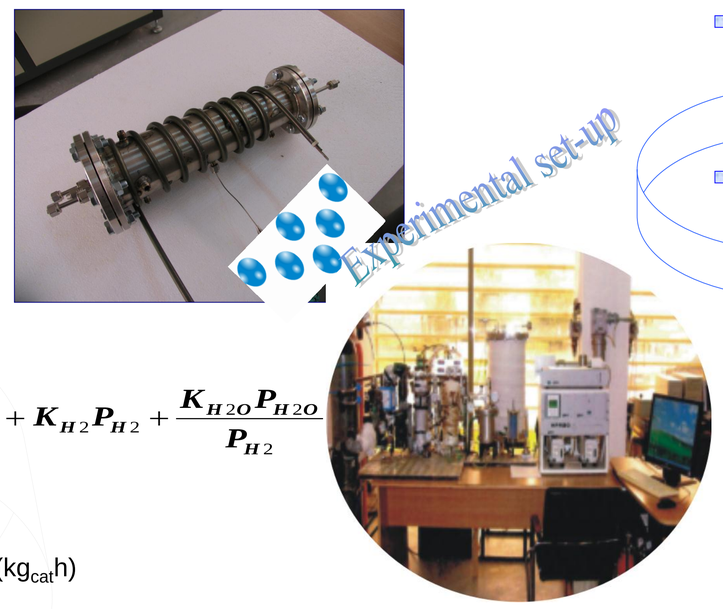


Figure 3. Temperature in the permeation zone



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 – light blue line)
For 420°K inlet temperature in the reforming area and as the wall temperature increases the temperature is increasing – dark blue line.
This occurs because the higher temperature in the reforming area promotes the steam methane reforming mechanism that consumes heat so the temperature decreases.

Future work

To validate the simulation results with experiments

Conclusions:

- A mathematical model approach for steam methane reforming in a membrane reactor has been developed.
- 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.
- An increase up to 398°K was noticed in the sweep (permeation) area, 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.

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