Modeling and Simulation of Hydrogen Generation In Membrane Reactor Via Steam Octane Reforming

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Introduction

Hydrogen is a necessary fuel for fuel cells to generate power for transportation. One conceivable way to produce hydrogen is through catalytic reforming of hydrocarbons via on-board reformers. Hydrogen is a major industrial product used in the production of many chemicals mainly, ammonia and methanol and food processing. Pure hydrogen is used in fuel cells. Efficient and economical methods of high-purity hydrogen production are needed. Producing hydrogen from coal can generate large volumes of this gas because coal is the words most plentiful fossil fuel [1]. The first reaction is strongly endothermic and the second reaction is exothermic. Equilibrium conversions of both reforming reactions benefit from high temperatures and low pressures [3,4]. By integrating the reaction and separation process in one-unit known as catalytic membrane reactor a significant improvement in the chemical conversion is observed [5]. Palladium-based membranes have been used as a component of catalytic membrane reactor technology. Different Pd and Pd-alloy membranes have been used under industrial situations, showing an outstanding concert [6] suitable for their application in large-scale settings.
Various hydrocarbon compounds have been converted into pure hydrogen by using a catalyst and a palladium membrane in one reactor (PMR) in a one-step process where the reaction proceeds to almost complete conversion. Octane is converted into pure hydrogen using of a palladium membrane reactor is described. Catalysts are used to endorse reactions such as methane steam reforming. These reactions only proceed to partial completion due to thermodynamic limitations. Consequently, a membrane, such as palladium, which is solely permeable to hydrogen, is merged into the reactor. Pure hydrogen moves to the permeate side enabling the reactions to proceed toward completion by maintaining a hydrogen-partial-pressure gradient across the membrane. Pure hydrogen is essential for use in fuel cell applications. In the present work, a mathematical model is used to describe the hydrogen generation using membrane reactor. The model equations are solved using COMSOL Multiphysics®. The effect of various operating parameters on membrane performance and octane conversion are investigated. The effect of the difference in membrane partial pressure in the permeate and retentate sections of the membrane and the ratio of steam to octane molar flow rate show significant effect on hydrogen generation. Reforming of gasoline, diesel, and their substitutes [7,8] has concerned much research because of their high-energy content and deep-rooted infrastructure for their supply and transport. Literature survey revealed that the amount of hydrogen produced from auto thermal reforming of jet fuel [10] or hexadecane [9] nearly reaches the yield at corresponding equilibrium conditions.

Governing Equations

Material balance
The steady state continuity equation for each species during the simultaneous mass transfer and chemical reaction in a reactive absorption system can be expressed as:

$$-\nabla N_i \pm r_i = V_z \frac{\partial C_i}{\partial z} \tag{1}$$

where N_i, r_i, V_z, C_i, and z are the flux, reaction rate of species *i*, velocity, concentration, and distance along the length of the membrane, respectively. The overall rate of reaction can be determined depending on the reaction mechanisms and reaction rates. The left-hand side of the above equation represents the diffusion and reaction terms, whereas the right-hand side of the equation is the convection term. The model is build up for non-wetting mode of operation (i.e. gas filled pores). The model equations for shell side, membrane side and tube side are as follows:

Shell side (Sweep gas compartment)

The steady state material balance for the transport of the sweep gas in the shell side may be written as follows ($i = N_2, H_2$):

$$D_{i,s}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{i.s}}{\partial r}\right)+\frac{\partial^2 C_{i,s}}{\partial z^2}\right]=\frac{\partial}{\partial z}\left(V_{zs}C_{i,s}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(rv_{rs}C_{i,s}\right) \quad (2)$$

Considering the active area around each fiber calculated from the hypothetical radius bearing in mind a hexagonal–shaped unit cell of the fiber assembly around each fiber.

Under countercurrent mode of operation, the following boundary conditions exist:

$$r = r_2,\ C_{i,s} = C_{i,m} \quad (4)$$

Identical concentration at the membrane-gas interface.

$$r = r_3,\ -\frac{\partial C_{i,s}}{\partial r} = 0, \quad (5)$$

axial symmetry at gas side hypothetical module radius.

$$z = 0,\ -\frac{\partial C_{i,s}}{\partial r} = 0 \quad (6)$$

Convective flux, outlet of gas stream.

$$z = L,\ C_{H_{2,s}} = C^{\circ}_{H_2},\ C_{C_8H_{18}} = C^{\circ}_{C_8H_{18}} \quad (7)$$

, inlet gas stream.

1.1.2 Membrane section

The steady state material balance for the transport of H_2 across the membrane skin layer for non-wetting mode of operation is due to diffusion only; no reactions are taking place in the gas filled pores

$$D_{i,m}\left[\frac{\partial^2 C_{i,m}}{\partial r^2}+\frac{1}{r}\frac{\partial C_{i,m}}{\partial r}+\frac{\partial^2 C_{i,m}}{\partial z^2}\right]=0 \quad (8)$$

Boundary conditions:
Membrane sweep interface

$$r = r_1,\ C_{i,m} = P(C_{i,t_i} - 0) \quad (9)$$

No flux on both sides for the membrane

$$z = 0,\ z = L,\ \frac{\partial C_{i,m}}{\partial z} = 0 \quad (10)$$

Thermal insulation at both ends of membrane.

Tube Side (reaction zone):

The steady state material balance for the transport of iso-octane in the tube side

$$D_{i,t}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{i,t}}{\partial r}\right)+\frac{\partial^2 C_{i,t}}{\partial z^2}\right]+r_{i,t}=\frac{\partial}{\partial z}\left(v_{zt}C_{i,t}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(rv_{rt}C_{i,t}\right) \quad (11)$$

where the subscript "*i*" indicates carbon monoxide, steam, hydrogen and carbon dioxide. Reaction rates for CO that takes place in the feed side [6,7]:
The steam reforming of isooctane is strongly endothermic and described by the reaction:

$C_8H_{18} + 8\,H_2O \rightarrow 8\,CO + 17H_2 \qquad \Delta H = 1275$ J/mol

The following expression found in the literature can be used to calculate the reaction rates of steam reforming over a Ni/Al_2O_3 catalyst:

$$r = \frac{k_{rxn}\, p_{C_8H_{18}}\, p_{H_2O}}{(1 + K_{C_8H_{18}}\, p_{C_8H_{18}} + K_{H_2O}\, p_{H_2O})^2} \quad (12)$$

The boundary conditions for gas flowing in lumen side of the fibers:
tube center, axial symmetry.

$$r = 0,\ -\frac{\partial C_{i,t}}{\partial r} = 0 \quad (13)$$

gas solubility in solvent at liquid-membrane interface

$$r = r_1,\ C_{i,t} = m_i C_{i.m} \quad (14)$$

solvent initial feed concentration.

$$z = 0,\ C_{C_8,H_{18}t} = C^{\circ}_{C_8H_{18}} \quad (15)$$

convective flux at the exit liquid stream.

$$z = L,\ -\frac{\partial C_{i,t}}{\partial z} = 0 \quad (16)$$

Use of COMSOL for Simulation

COMSOL 5.3 Graphical User Interface is used to construct
(1) the surface plot of the mass fraction of hydrogen within the microchannel and

(2) to plot the molar fraction of hydrogen as a function of the reactor's length in the middle of the microchannel.

In the Model Navigator select a 2D coordinate system and click on the option Steady-state analysis of the application mode Diffusion through diluted species within the balance of the Chemical Engineering Module.

Simulation Results / Discussion

Steam reforming of iso-octane is carried out in a tubular reactor without membrane. Figure 1 depicts the mass fraction of hydrogen generated with the reactor. Figure 2 represented the velocity profile in the reactor. The figure shows that the velocity is fully developed after 0.015 m of the tube. That's is attributed to the velocity. This distance can be increased or decreased based in the velocity.

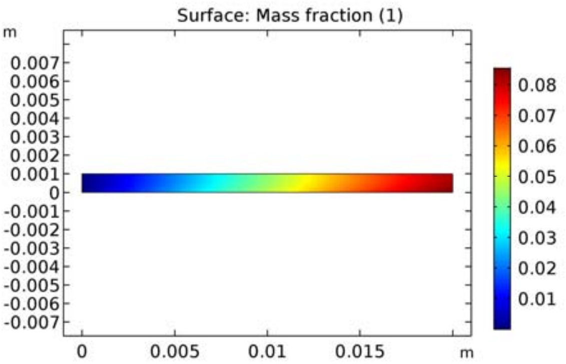

Figure 1. The generated hydrogen mass fraction in the reactor without membrane.

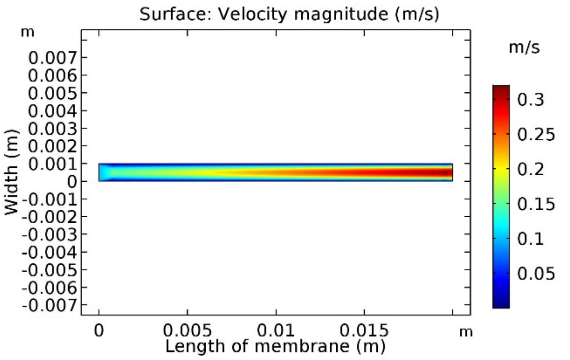

Figure 2. The velocity profile in tube where reaction is taking place

The conversion of iso-octane along the membrane length is shown in Figure 3. The conversion of 0.75 is achieved using the reactor without membrane.

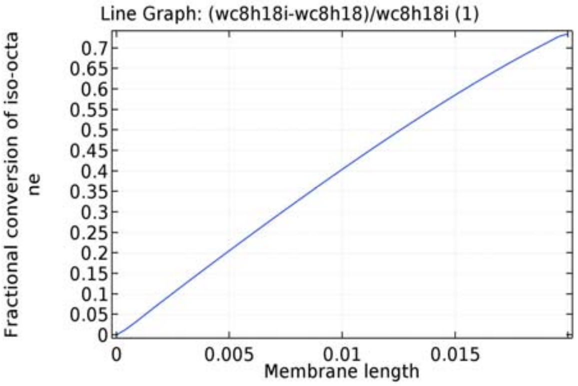

Figure 3 Iso-octane conversion in the absence of membrane and sweep gas

In the second case membrane is inserted in the shell side and a sweep gas compartment is added to sweep the hydrogen crossing the membrane barrier. Figure 4 represents a membrane reactor with sweep gas booth, the sweep gas in this case is nitrogen. The figure shows that most there do exit a hydrogen in the sweep gas compartment.

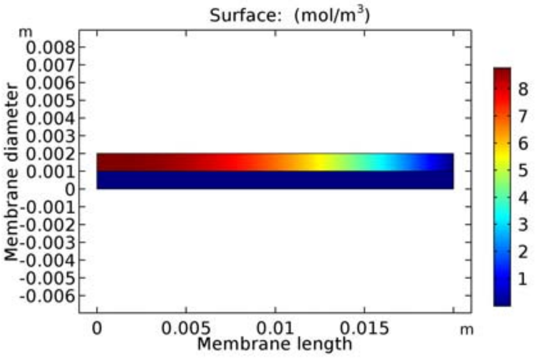

Figure 4. The concentration of hydrogen inside the reactor with membrane and sweeping nitrogen gas

The iso-octane conversion in the present of membrane and sweep gas compartment is shown in Figure 5. The figure revealed that there is slight increase in conversion in present of membrane. The hydrogen diffuses through the membrane walls to the sweep gas.

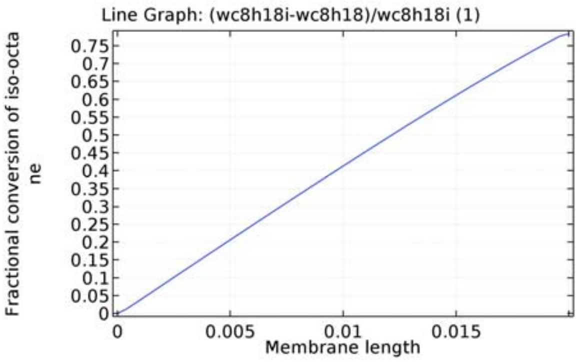

Figure 5. Conversion of iso-octane using membrane reactor

Figure 6 shows the hydrogen concentration in the reactor zone. The hydrogen concentration is decreases toward the membrane side.

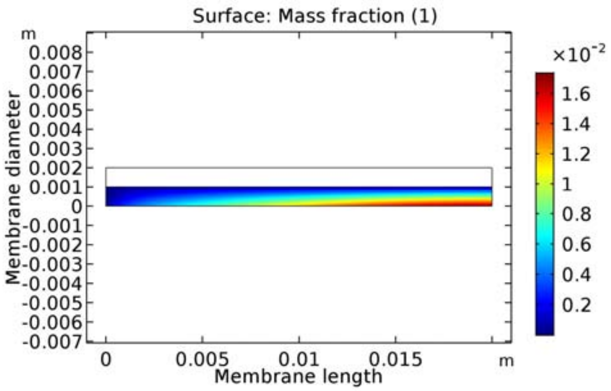

Figure 6. Hydrogen concentration in the reactor zone in the presence of membrane reactor

Conclusions

Steam reforming of iso-octane in a monolithic type reactor was simulated by a three-dimensional computational fluid dynamics model. The variations of hydrogen production and reactor temperature along the length of the reactor were calculated at isothermal, adiabatic and constant heat flux conditions. A 2-D model was developed to demonstrate the isooctane steam reforming in a membrane reactor to simulate steam reforming of iso-octane was developed. The model equations were solved using COMSOL. A comparison of the case in present and without membrane shows that the present in membrane increased the conversion of iso-octane.

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Acknowledgements

The authors are thankful to the UAE University Deanship of Scientific Research that provided the grant no. 31N168-UPAR (9) 2013