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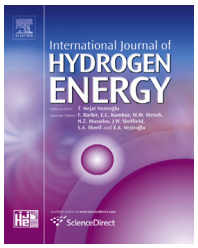

Simulation of hydrogen and propylene coproduction in catalytic membrane reactor

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ABSTRACT

A two-dimensional non isothermal mathematical model has been developed to simulate the propane dehydrogenation in a catalytic membrane reactor with tube-and-shell configuration. The permeable inner tube consists of an inert large-pore support and thin microporous membrane layer. The membrane removes hydrogen from reaction zone shifting the reaction equilibrium towards products. Both pores diameter and membrane thickness were varied to obtain the optimal membrane characteristics in terms of hydrogen and propylene productivity, and hydrogen purity. The model correctly predicted the improved process parameters when the membrane thickness was 4 μm and the pore diameter was 0.4 nm.

Introduction

Today many different techniques have been used for hydrogen production [1,2]. The following paths can be mentioned concerning hydrogen production: steam reforming of methane and natural gas [3–5], gasification of biomass [6,7] and etc. An alternative way is the dehydrogenation of alkanes with production of alkenes and hydrogen. To obtain the relatively pure hydrogen the separation procedure is required.

On the other hand, light olefins are important chemicals in organic synthesis because of their high chemical activity in certain reactions. Propylene is the one of the most valuable petrochemicals. The traditional processes for propylene production suffer from thermodynamic limitations, coke formation and require costly heat exchange at high operating temperatures because of the endothermicity of the reaction.

The traditional catalytic dehydrogenation is thermodynamically limited and requires very high temperatures (over 700 °C) to achieve a high enough conversion of propane. In addition, it has such disadvantages as the deactivation of the catalyst by coke formation, and the consequent need for continuous or periodic catalyst regeneration at frequent intervals throughout the process. While the propane conversion may be increased by operating at higher temperatures, that in its turn induces an increase in the rate of catalyst deactivation and a decrease in the reaction selectivity towards propylene.

In the last several decades, inorganic catalytic membrane reactors (CMR) have attracted extensive attention in the research community [8–10]. The use of a membrane allows one to remove selectively a product from reaction zone, shifting the reaction equilibrium towards the product side and simplifying subsequent product separations [11,12].

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In this paper the propane dehydrogenation process was considered as an example. Propane dehydrogenation in the catalytic membrane reactor may be a potential method for increasing conversion while maintaining acceptable catalyst deactivation rate and reaction selectivity [13]. The essential benefit of integrating a selective membrane in the reactor is referring to higher propylene yield at lower temperatures in comparison with traditional catalytic dehydrogenation [14].

Thus, the application of the CMR permits one to combine the hydrogen and propylene production with separation in one reactor. In order to develop an effective membrane reactor, we have carried out the theoretical analysis and optimization of membrane characteristics in terms of their impact on process effectiveness.

Mathematical modeling

The membrane reactor scheme is represented by Fig. 1. It consists of two concentric tubes. The interior ceramic tube is filled with the fixed bed catalyst which is active in propane dehydrogenation reaction. A microporous oxide membrane covers the ceramic tube from the shell side. Depending on membrane pore size, hydrogen and other components of reaction mixture can permeate through the membrane to the shell compartment. Flow of inert sweep gas removes the permeated components from the shell side of reactor away. Selective hydrogen removal from the reaction zone shifts the reaction equilibrium towards the products increasing hydrogen and propylene yields. From other hand, relatively pure hydrogen can be obtained in the shell side of membrane reactor.

The developed mathematical model allows one to analyze the concentration profiles of all components in the reaction mixture as well as the propane conversion in terms of their distribution by the length of reactor. The equations of mass and energy balances are given below.

Mass balances

Tube side: $0 < r_1 < R_1$

$$\frac{\partial\left(u_l^t C_i^t\right)}{\partial l} = \varepsilon^t \frac{1}{r_1}\frac{\partial}{\partial r_1}\left(r_1 D_{e_i}^t \frac{\partial C_i^t}{\partial r_1}\right) + \rho_k^t(1-\varepsilon^t)\times\sum_{j=1}^{N_R}\gamma_{ij}w_j, \quad \forall i \tag{1}$$

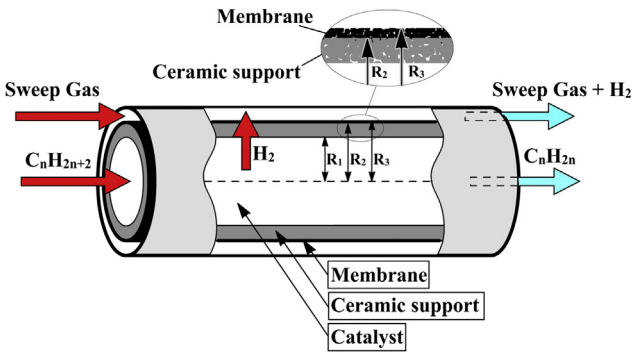

Fig. 1 – The scheme of the membrane reactor.

Boundary conditions:

$$l = 0:\ C_i^t = C_{in}^t;\ r_1 = 0:\ \frac{\partial C_i^t}{\partial r_1} = 0 \tag{2}$$

At the boundary ***tube/ceramic support:***

$$r_1 = R_1:\ C_i^t = C_i^c;\ D_{e_i}^t \varepsilon^t \frac{\partial C_i^t}{\partial r_1}\bigg|_{r_1=R_1} = D_{e_i}^c \varepsilon^c \frac{\partial C_i^c}{\partial r_2}\bigg|_{r_2=R_1}, \quad \forall i \tag{3}$$

Ceramic support: $R_1 < r_2 < R_2$

$$\frac{\varepsilon^c}{r_2}\frac{\partial}{\partial r_2}\left(r_2 D_{e_i}^c \frac{\partial C_i^c}{\partial r_2}\right) = 0, \quad \forall i \tag{4}$$

Boundary conditions:

At the boundary ***ceramic support/tube:*** the boundary conditions are the identical to those for *tube/ceramic support*.

At the boundary ***ceramic support/membrane:***

$$r_2 = R_2:\ C_i^c = C_i^m;\ D_{e_i}^c \varepsilon^c \frac{\partial C_i^c}{\partial r_2}\bigg|_{r_2=R_2} = D_{e_i}^m \varepsilon^m \frac{\partial C_i^m}{\partial r_3}\bigg|_{r_3=R_2}, \ \forall i \tag{5}$$

Membrane: $R_2 < r_3 < R_3$

$$\frac{\varepsilon^m}{r_3}\frac{\partial}{\partial r_3}\left(r_3 D_{e_i}^m \frac{\partial C_i^m}{\partial r_3}\right) = 0, \quad \forall i \tag{6}$$

At the boundary ***membrane/ceramic support:*** the boundary conditions are the identical to those for *ceramic support/membrane*.

At the boundary ***membrane/shell***:

$$r_3 = R_3:\ D_{e_i}^m \varepsilon^m \frac{\partial C_i^m}{\partial r_3}\bigg|_{r_3=R_3} = \beta\left(C_i^s - C_i^m\right), \ \forall i \tag{7}$$

Shell side:

$$\frac{\partial\left(u_l^s C_i^s\right)}{\partial l} = \beta\left(C_i^m - C_i^s\right), \ \forall i \tag{8}$$

Boundary conditions:

$$l = 0:\ C_i^s = 0,\ i = 1,\ N_t - 1 \tag{9}$$

Energy balance

Tube side: $0 < r_1 < R_1$

$$\rho_G^t c_p^t u_l^t \frac{\partial T^t}{\partial l} = \frac{1}{r_1}\frac{\partial}{\partial r_1}\left(\lambda_{ef}^t r_1 \frac{\partial T^t}{\partial r_1}\right) + \rho_k^t(1-\varepsilon^t)\times\sum_{j=1}^{N_R} w_j\left(-\Delta H_j\right) \tag{10}$$

Boundary conditions:

$$l = 0:\ T^t = T_{in}^t;\ r_1 = 0:\ \frac{\partial T^t}{\partial r_1} = 0 \tag{11}$$

At the boundary ***tube/ceramic support:***

$$r_1 = R_1:\ T^t = T^c,\ \lambda_{ef}^t \frac{\partial T^t}{\partial r_1}\bigg|_{r_1=R_1} = \lambda^c \frac{\partial T^c}{\partial r_2}\bigg|_{r_2=R_1} \tag{12}$$

Ceramic support: $R_1 < r_2 < R_2$