

Theoretical Study of Palladium Membrane Reactor Performance During Propane Dehydrogenation Using CFD Method

Kamran Ghasemzadeh*, Milad Mohammad Alinejad, Milad Ghahremani, Rahman Zeynali, and Amin Pourgholi

Chemical Engineering Department, Urmia University of Technology,
Urmia 57155, West Azarbayjan, Iran

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ABSTRACT

This study presents a 2D-axisymmetric computational fluid dynamic (CFD) model to investigate the performance Pd-Ag membrane reactor (MR) during propane dehydrogenation process for hydrogen production. The proposed CFD model provided the local information of temperature and component concentration for the driving force analysis. After investigation of mesh independency of CFD model, the validation of CFD model results was carried out by other modeling data and a good agreement between CFD model results and theoretical data was achieved. After model validation, the effects of the important operating parameter (reaction temperature) on the performances of membrane reactor (MR) were studied in terms of propane conversion and hydrogen yield. The CFD results showed that the suggested MR system during propane dehydrogenation reaction presents a higher performance with respect to once obtained in the conventional reactor (CR). In particular, by applying Pd membrane, was found that propane conversion can be increased from 41% to 49%. Moreover, the highest value of propane conversion ($X = 91\%$) was reached in case of Pd-Ag MR. It was also established that the feed flow rate of the MR is to be one of the most important factors defining efficiency of the propane dehydrogenation process.

Keywords: hydrogen production; Computational Fluid Dynamic; Modeling; propane dehydrogenation; membrane reactor

ABSTRAK

Kajian ini menyajikan model komputasi dinamika fluida (KDF) axisimetri dua dimensi untuk menyelidiki unjuk kerja reaktor membran Pd-Ag (RM) selama proses dehidrogenasi propana untuk produksi hidrogen. Model KDF yang diusulkan mencakup informasi lokal tentang temperatur dan konsentrasi komponen untuk analisis gaya pengarahannya. Setelah kajian kebebasan ukuran model KDF, hasil validasi model KDF diperoleh dari pemodelan yang lain dan suatu kesepakatan kuat antara hasil model KDF dan data teoritis akan diberikan. Setelah validasi model, pengaruh parameter operasi yang penting (temperatur reaksi) pada unjuk kerja RM dipelajari berdasarkan konversi propana dan hidrogen yang dihasilkan. Hasil KDF menunjukkan bahwa sistem RM yang digunakan selama reaksi dehidrogenasi propana menggambarkan unjuk kerja yang relatif lebih bagus dibandingkan reaktor konvensional (RK). Secara umum, penerapan membran Pd akan menghasilkan konversi propana yang meningkat dari 41 % menjadi 49%. Selanjutnya, nilai konversi propana tertinggi ($X = 91\%$) dihasilkan pada penggunaan Pd-Ag. Hal ini juga membuktikan bahwa laju alir umpan pada RM menjadi satu faktor terpenting untuk menentukan efisiensi proses dehidrogenasi propana

Kata Kunci: produksi hidrogen; komputasi dinamika fluida; pemodelan; dehidrogenasi propana; reaktor membran

INTRODUCTION

Nowadays the world demand of propene is fast increasing [1-3] because of the heavy increase in the demand of polypropylene, acrylonitrile, propene oxide, cumene, phenol, isopropyl alcohol and many other propene derivatives. The propene obtained as a co-product from steam crackers or Face Centered Cubic (FCC) units does not satisfy the growing demand. Consequently, there is a great interest in developing

alternative routes for propene production. Propane dehydrogenation is one of the techniques for on-purpose propene production, and several propane dehydrogenation processes, such as Oleflex and Catofin, have been commercialized.

Propane dehydrogenation is equilibrium limited and highly endothermic, which is usually carried out at 500-600 °C and atmospheric pressure on platinum or chromium catalysts.

* Corresponding author.
Email address : kamran.ghasemzadeh@uut.ac.ir

Alternatively, the direct dehydrogenation of propane (see Eq.1) represents an efficient route to propene:



Up to now, investigation on the reaction of propane dehydrogenation has been mainly focused on improving the catalytic performance. However, some efforts have been devoted to applying MR system during propane dehydrogenation. Indeed, the use of the MR permits one to combine the advantages of conventional dehydrogenation and separation processes. In this case, the propane undergoes the dehydrogenation reaction over the catalyst in the shell side and hydrogen permeates through the membrane to the tube compartment. It should be noted that selective hydrogen removal through the membrane allows one to shift the reaction equilibrium towards the desired products [2-3].

There are few works [4-16] devoted to mathematical modeling of various processes in the Pd-based MR. However, in most cases, the existing models are not capable of describing the full distribution of heat and mass transfer processes taking place in MR. In recent years, CFD method as a useful tool has indicated key rules in improving model validation. However, there is no any CFD analysis about propane dehydrogenation in Pd-Ag MR system. On the other hand, concerning to Pd-Ag membrane technology progress, this type of membrane can use as good option for hydrogen removal during propane dehydrogenation. Therefore, in this study, a CFD model was presented to the analysis of Pd-Ag MR performance with respect to CR during propane dehydrogenation.

MODEL DEVELOPMENT

Membrane Reactor Configuration

A 2D-axisymmetric, isothermal model was developed using CFD method to simulate the performance of a dense Pd-Ag MR and CR. Fig.1 shows the scheme of Pd-Ag MR for hydrogen production during propane dehydrogenation reaction.

The main assumptions of this model are:

Steady state condition.

Isothermal condition.

Physical properties, such as gas density, are constant with temperature.

The reaction occurs only at the catalyst surface, so there is no mass transfer resistance between the bulk gas and the catalyst surface.

The film transport resistance supposed at the interface of gas/membrane was considered negligible.

A pseudo-homogenous condition in the reaction zone.

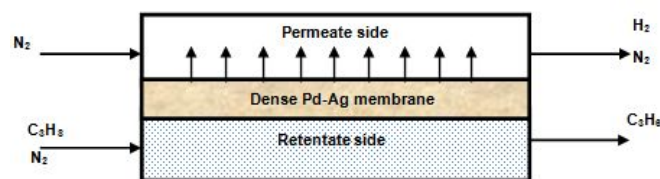


Fig 1. A schematic of the 2 dimensional simulated Pd-Ag MR during propane dehydrogenation

The last assumption means that the catalyst surface and bulk fluid have the same conditions and, as a result, the behavior of both phases can be considered by the same variables.

Governing Equations

The main equations used in this model is presented in the following:

Mass balance equation for reaction side

$$\frac{dN_i}{dZ} = \frac{W}{V} \sum_{j=1}^5 V_{ij} r_j - J_i \frac{\pi D}{A} \quad (1)$$

Mass balance equation for permeate side

$$\frac{dN_i}{dZ} = \pm J_i \frac{\pi D}{A} \quad (2)$$

r_i is the reaction rate with a corresponding stoichiometric coefficient ν_i , N_i is the molar flow rate of each component.

Pressure drop equation

$$\frac{dp}{dz} = 150 \frac{\mu U}{d_p^2} (1-\epsilon)^2 + \frac{7 \rho_{\text{gas}} V^2}{4 d_p} \frac{1-\epsilon}{\epsilon} \quad (3)$$

where p is the pressure, ϵ the catalyst bed porosity, d_p the catalyst diameter, U the gas velocity, μ the gas viscosity and ρ_{gas} the gas density.

Membrane flux

On the other hand, the laws regulating the hydrogen permeation flux through the dense Pd-Ag membrane are described below:

$$J_{\text{H}_2} = \frac{Pe}{\delta} (p_{\text{H}_2, \text{retentate}}^{0.5} - p_{\text{H}_2, \text{permeate}}^{0.5}) \quad \text{Fick - Sieverts law} \quad (4)$$

where J_{H_2} is the hydrogen permeating flux through the Pd-Ag membrane, δ the membrane thickness, $p_{\text{H}_2, \text{retentate}}$ the hydrogen partial pressure in retentate side, $p_{\text{H}_2, \text{permeate}}$ the hydrogen partial pressure in permeate side and Pe the hydrogen permeability that is defined by the following equation:

$$Pe = Pe_0 \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

Reaction rate

The expression of propane dehydrogenation reaction rate, kinetics, and equilibrium parameters have been taken from Shelepova et al. [1] as following:

$$r_{\text{PDH}} = \frac{k_1 (P_{\text{C}_3\text{H}_8} - P_{\text{C}_3\text{H}_6} P_{\text{H}_2} / K_{\text{eq}})}{1 + K_{\text{C}_3\text{H}_6} P_{\text{C}_3\text{H}_6}} \quad (6)$$

$$k_1 = k_{01} \times \exp\left(\frac{-E_{a1}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right) \quad (7)$$

$$K_{C_3H_6}^* = \frac{1}{K_{C_3H_6}} = \frac{1}{K_0 \cdot \exp\left(\frac{-\Delta H_{C_3H_6}}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right)} \quad (8)$$

where k_1 and K_{eq} are the reaction rate and equilibrium constants for reaction, respectively; $K_{C_3H_6}^*$ the adsorption coefficient for C_3H_6 , T and T_m are a reaction and reference temperatures, respectively, and E_a activation energy. In this case, Table 1 provides the kinetics parameters values used inside the model.

Post Processing Definitions

The following definitions were used for describing the dense Pd-Ag MR and CR performance:

$$\text{Propane -Conversion}(\%) = \frac{C_3H_{8in} - C_3H_{8out}}{C_3H_{8in}} \times 100 \quad (9)$$

where C_3H_{8in} is the propane molar feed flow rate and C_3H_{8out} the propane flow rate in the reactor outlet,

$$\text{Hydrogen recovery} (\%) = \frac{H_{2-permeate}}{(H_{2-permeate} + H_{2-retentate})} \times 100 \quad (10)$$

where $H_{2-permeate}$ is the hydrogen molar flow rate that permeates through the membrane and $H_{2-retentate}$ the hydrogen molar flow rate in retentate side. It should be noted that the eq.10 is related to the MR simulation.

Numerical Method

Numerical simulations were performed using the commercial CFD package COMSOL Multiphysics 5.2.1 the finite-element method was used to solve the governing equations in the two-dimensional CFD model for present work. Moreover, the pressure-velocity correction was done using the SIMPLE algorithm. Dependencies of fluid density, viscosity, diffusivity, thermal conductivity and heat capacity of temperature, pressure, and composition were accounted for using standard definitions defined in the computation software. A small fraction of H_2 at the reaction zone entrance was used to prevent numerical problems that shoot from the appearance of hydrogen partial pressure in the denominator in equations of (4) and (5). Furthermore, the solution was considered achieved when the residuals converged to values less than the magnitude of 10^{-4} and all the variable values were not changed with iteration.

RESULT AND DISCUSSION

In present work, a CFD study has been carried out for comparing the effect of most important operating conditions on the performances in terms of propane

Table1. Values rates and equilibrium constants used in this model

Parameters	Values	Unites
k_{01}	6.12×10^{-2}	$\text{mmols}^{-1} \text{gr}^{-1} \text{bar}^{-1}$
E_{a1}	34.57	kJmol^{-1}
k_0	3.46	bar
$\Delta H_{C_3H_6}$	-85.817	kJmol^{-1}
T_m	793	K

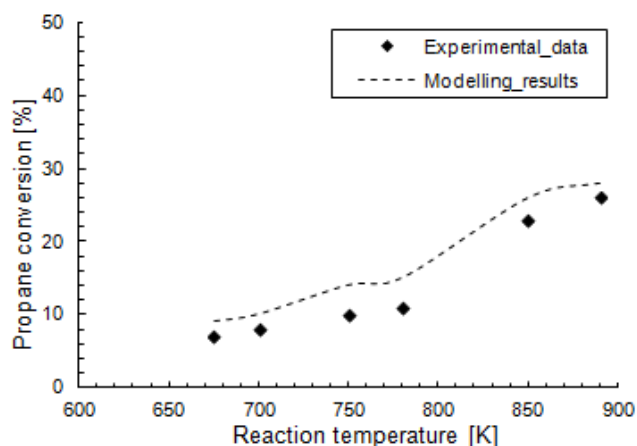


Fig 2. Comparison of CFD modeling results and experimental data in the CR during propane dehydrogenation reaction (in term of propane conversion)

conversion and hydrogen recovery of the MR equipped with dense Pd-Ag during dehydrogenation. In particular, effects of reaction temperature and feed flow rate were investigated during mentioned reaction after model results validation.

Model Validation

The accuracy of our CFD model was verified versus experimental data measured by Sheintuch et al. [15-16]. Fig. 2 shows the propane conversion versus reaction temperature for the CR during propane dehydrogenation reaction. It should be noted that there is no experimental data for the case of MR.

The operating conditions for the CR model were considered similar to experimental work at a reaction pressure of 6 bar and feed flow rate of 0.75 L/min. It can be seen that the simulated values are in a good agreement with the reported experimental values. A comparison between numerical and experimental results reveals that the error ranges between 3 and 5%.

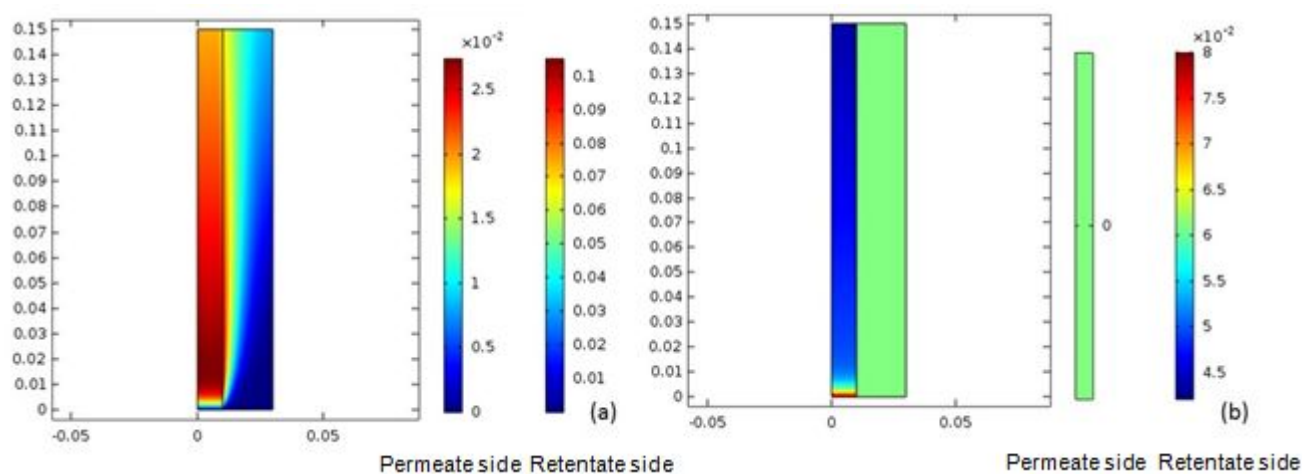


Fig 3. Concentration [mol/m^3] distribution of H_2 (a) and C_3H_8 (b) in the Pd-Ag MR

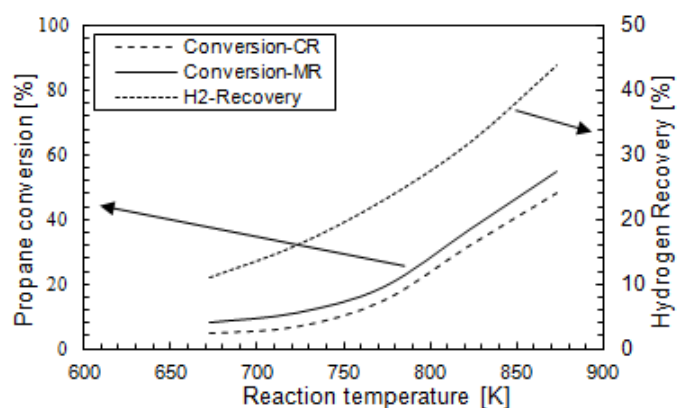


Fig 4. Propane conversion and hydrogen recovery versus reaction temperature for both of the dense Pd-Ag MR and CR (at reaction pressure of 1 bar and feed flow rate of 0.5 L/min)

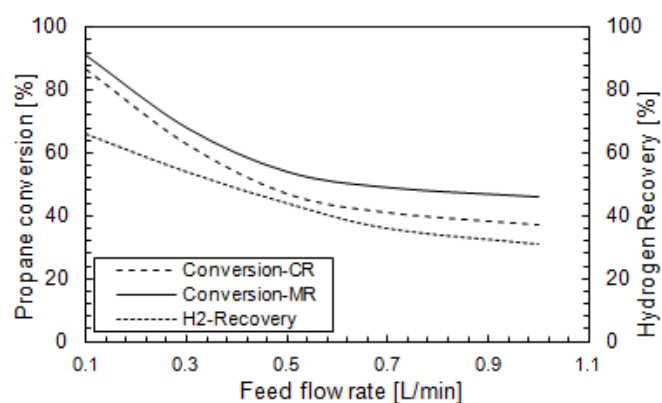


Fig 5. Propane conversion and hydrogen recovery versus feed flow rate for both of the dense Pd-Ag MR and CR (at reaction pressure of 1 bar and reaction temperature of 873 K)

Evaluation of Pd-Ag MR Performance

Before the comparative analysis of propane dehydrogenation reaction for hydrogen production in the Pd-Ag MR, several typical CFD results for showing the distribution of velocity, pressure, and components concentration are studied. Hence, Fig. 3 presents typical results, showing simulated contours of the H_2 and C_3H_8 concentration within the computation domain during propane dehydrogenation reaction for feed flow rate of 0.75 L/min, the feed pressure of 1 bar and reaction temperature of 773 K. These plots clearly justify the use of the 2D model since strong radial gradients develop, leading to relatively low H_2 partial pressures at the membrane vicinity in the reaction zone. Since the driving force for H_2 separation is determined by the difference in H_2 partial pressures on both sides of the dense Pd-Ag membrane, more H_2 permeance can be achieved by using sweep gas stream in permeate side and

consequently, the overall performance of the MR in terms of C_3H_8 conversion and H_2 recovery can be improved. Moreover, as shown in Fig. (3b), the C_3H_8 consumption was clearly validated in the length of the reaction zone.

Reaction Temperature Effect

The influence of reaction temperature on the MR performance during dehydrogenation reaction in terms of propane conversion and CO_x -free hydrogen recovery was evaluated.

Hence, Fig. 4 indicates propane conversion and hydrogen recovery versus reaction temperature. As shown in this figure, Owing to the endothermic character of the propane dehydrogenation reaction system, propane conversion is increased by enhancement of the reaction temperature. Indeed, with regard to the Pd-Ag MR performance, an increase in propane conversion with temperature is also due to the

reaction products removal from the reaction zone through the membrane. In this condition, an achievable propane conversion using the Pd-Ag MR will be higher than the ones related to the CR.

Furthermore, as indicated in Fig. 4, an enhanced hydrogen recovery is obtained by increasing the temperature in the dense Pd-Ag MR during propane dehydrogenation reaction and this effect is related to Sievert mechanism of the Pd-based membrane, in which membrane permeance will be increased by temperature enhancement.

Feed Flow Rate Effect

Another important operating parameter, taken into account in this work, is the feed flow rate. The influence of feed flow rate on the Pd-Ag MR performance in terms of propane conversion and hydrogen recovery was evaluated. In this case, the simulations were accomplished at 1 bar and 873 K by varying the feed flow rate between 0.1 and 1 L/min. As illustrated in Fig. 5, the propane conversion decreases by increasing the feed flow rate for the dense Pd-Ag MR and CR. By decreasing the feed flow rate, a higher residence or contact time in the reaction zone is favored. In fact, the lower values of feed flow rate can favor to hydrogen formation in reaction side. This effect produces a higher retentate hydrogen partial pressure that enhances the hydrogen permeation driving forces with a consequent more effective shifting of the propane dehydrogenation reaction towards the products. Therefore, this gives more propane consumption and a greater hydrogen production as well as a higher hydrogen stream permeating through the membrane. Thus, lower feed flow rate is more effective for higher propane conversion, hydrogen production and, then, for higher hydrogen recovery (see Fig. 5).

CONCLUSION

In this study, a quantitative study on Pd-Ag MR performance for hydrogen production during propane dehydrogenation was carried out. To perform quantitative aspect as a first approach, the CFD method was used to simulate a Pd-Ag MR performance. The model validation of CR was carried out by using the experimental data of Sheintuch et al. [15] reaching a good agreement with modeling results. After model validation, this study was focused on the analysis of the Pd-Ag MR performance during propane dehydrogenation in terms of propane conversion and hydrogen recovery by varying reaction temperature and feed flow rate as most important operating parameters. The model results indicated that increasing the reaction temperature and decreasing the feed flow rate have

positive effects on MR and CR performance. Moreover, in all operating condition, Pd-Ag MR presented a better performance (around 7%) with respect to CR.

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