

## Investigation of isobutane dehydrogenation in silica membrane reactor based on CFD method

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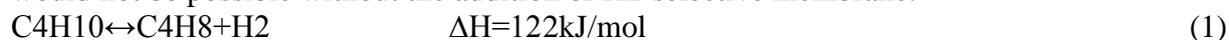
### Abstract

This study presents a 2D computational fluid dynamic (CFD) to investigate the performance of silica membrane reactor (MR) during isobutane dehydrogenation reaction for hydrogen and isobutene production. The proposed CFD model provides the local information of velocity and component concentration for the driving force analysis. The validation of model results was carried out by experimental data and a good agreement between model results and experimental data was achieved. In MR model, a commercial Pt/Al<sub>2</sub>O<sub>3</sub> catalyst in reaction zone was considered. The effects of some important operating parameters such as reaction temperature and reaction pressure on the performance of silica MR were studied in terms of isobutane conversion and hydrogen recovery. The CFD results showed that the silica MR during isobutane dehydrogenation reaction presents higher performance in terms of isobutane conversion and hydrogen recovery with respect to Packed-bed reactor (PBR), in all the studied cases.

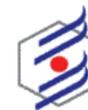
**Keywords:** isobutane, dehydrogenation, membrane reactor, hydrogen recovery

### 1. Introduction

Isobutylene is an important intermediate for synthetic rubber, plastics, and various chemical and petrochemical products such as methyl tert-butyl ether, alkylate gasoline, and butyl rubber [1]. The most popular industrial technique to synthesize isobutylene is catalytic dehydrogenation of isobutane [2]. A dehydrogenation reaction requires relatively high operating temperature for achieving high yield in a conventional reactor. Rigorous operating conditions results in inevitable catalyst deactivation because of coke formation [3–7]. However, in packed bed membrane reactors (PBMR), the membrane assists in moving equilibrium towards the forward reaction due to selective H<sub>2</sub> removal across the membrane (Eq. 1). For this reason, the PBMR is capable of exceeding the equilibrium limitations, which would not be possible without the addition of H<sub>2</sub>-selective membrane.



Isobutane dehydrogenation using catalytic MR has been studied previously by a number of researchers. Ionnides and Gavalas [8] used a dense silica membrane reactor and obtained increases in selectivity and yield over a fixed bed reactor (FBR) at higher space times. Matsuda et al. [9] employed a palladium MR and tested both a chromia/alumina and a platinum alumina catalyst. The isobutene yield for both was greater than for a conventional reactor. Bernald et al. [10] used a membrane reactor with a very thin palladium film, while



Casanave et al. used both microporous and zeolite membrane reactors for this reaction [11]. Further zeolite MR results by Ciavarella et al. [12] discussed the effect of operating conditions. Moreover, concerning to high cost of experimental works, numerical models [13, 14] could be useful to avoid high experimental costs and to develop a better understanding of the effects of various parameters for the design and study of silica MRs in the isobutane dehydrogenation and also specific features and constraints like the necessity of obtaining a high purity hydrogen stream. To this purpose, computational fluid dynamic (CFD) tool is a feasible method to simulate detailed gas flow characteristics at any point of a membrane system. Indeed, the CFD approach can be used for virtual prototyping of chemical reactors and separators and since it is based on control volume methodology, the local variations of the fluid, thermal and mass transport properties can be visualized in comparison to simple models and can be used to design the MRs [15].

In the present work, as a first approach, a silica MR performance was modeled using the CFD method to investigate effects of the most important operating parameters in comparison with the PBR system during the isobutane dehydrogenation reaction. Then, A set of simulation results is provided illustrating some significant points about the silica MRs performance in terms of isobutane conversion and hydrogen recovery for isobutane dehydrogenation.

## 2. Development of CFD model

Fig. 1 shows a simple scheme of silica MR performance for hydrogen production during isobutane dehydrogenation reaction.

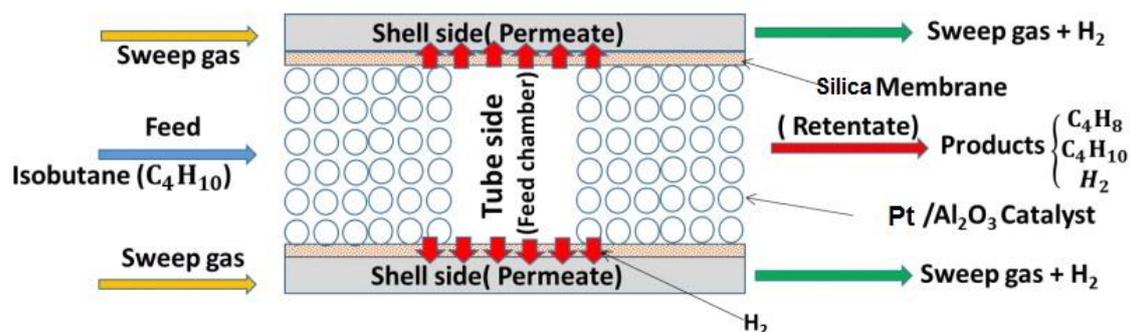


Fig. 1. Schematic of Packed-bed catalytic MR for isobutane dehydrogenation.

Moreover, the main assumptions of this CFD model are summarized as follows:

- (1) Isothermal conditions;
- (2) plug flow in both the feed and permeate sides;
- (3) No axial or radial diffusion;
- (4) Permeation through the membrane is proportional to the difference in partial pressures between the feed and permeate sides;
- (5) Dehydrogenation reactions take place only on the catalysts packed in the feed side.

### 2.1. Governing equations

Briefly, the CFD model is mathematically expressed by the governing equations consisting of continuity equation (Eq. (2)), momentum balance (Eq. (3)) and species transport reaction equation (Eq. (4)):

$$\nabla(\rho_f \cdot \varepsilon \cdot \mathbf{u}) = 0 \quad (2)$$

$$\nabla(\rho_f \cdot \mathbf{u} \cdot \mathbf{u} \cdot \varepsilon) = -\nabla p - \beta \mathbf{u} + \nabla \tau + \rho_f \mathbf{g} \quad (3)$$



$$\nabla(\rho_f \cdot u_i \cdot \varepsilon) = \nabla(\rho_f D_{i,e} \nabla m_i) + (1-\varepsilon)\rho M_i \sum_j v_{ij} R_j \quad (4)$$

In the equations above,  $m_i$  is the mass fraction of species  $i$ ,  $R_j$  is the reaction rate with a corresponding stoichiometric coefficient  $v_{ij}$  and  $\varepsilon$  is the void fraction of the packed bed. Moreover,  $\beta$  is the friction coefficient given by the following equation:

$$\beta = \frac{150\mu_f(1-\varepsilon)^2}{\varepsilon \cdot d_p^2} + \frac{1.75(1-\varepsilon)\rho_f}{\varepsilon^3 d_p} |u| \quad (5)$$

where  $m_i$  is the mass fraction of species  $i$ ,  $R_j$  the reaction rate with a corresponding stoichiometric coefficient  $v_{ij}$ ,  $\varepsilon$  the void fraction of the packed bed and  $S_{H_2}$  the source/sink term of hydrogen component. For the reaction zone (Fig.1), which is packed with catalyst pellets, the model includes the reaction terms ( $R_j$  denotes the rate of a reaction  $j$ ), the sink term ( $S_{H_2}$ ) that accounts for  $H_2$  removal by the membrane, and the friction term ( $\beta \cdot u$ ) to account for pressure losses along the packed bed. There is no catalyst in the permeate zones ( $\varepsilon=1$ ) and, therefore, there is no reaction there ( $R_j=0$ ). The source/sink term that accounts for mass flow of  $H_2$  across the dense Pd-based membrane is given by Eq.(6), in which the  $H_2$  flux is given by Sieverts' law, Eq. (7) ( $P_{H_2,retentate}$  and  $P_{H_2,permeate}$  are the partial pressures for hydrogen in the retentate and permeate sides, respectively)[16].

$$S_j = \frac{A_m J_j M_i}{V} \quad (6)$$

$$J_{H_2} = \frac{P e_0 \exp\left(\frac{-E_{H_2}}{RT}\right) (P_{H_2,retentate} - P_{H_2,permeate})}{\delta} \quad (7)$$

Where  $\delta$  is membrane thickness and  $P_e$  the hydrogen permeability that is defined by the following equation, in which,  $E_a=8.78$  kJ/mol,  $P_{e0}=2.72 \times 10^{-6}$  mol/m s Pa

The isobutane dehydrogenation equilibrium reaction is same as Eq.(1). The rate expression for this reaction was given by Dangwal et al. [17]. The following reaction rate equation of isobutane dehydrogenation,  $r_{isobutane}$ , was used for CFD modeling:

$$r = k \cdot (P_{C_4H_{10}} - P_{C_4H_8} \cdot P_{H_2} / K_{eq}) \quad (8)$$

$$k = 8.43 \cdot 10^{-12} \exp\left(-\frac{28190 \left[\frac{J}{mol}\right]}{RT}\right) \quad (9)$$

$$K_{eq} = 1128 \cdot \exp\left(-\frac{9327}{T}\right) \quad (10)$$

The following correlations were defined for describing the dense Pd-based MR performance in isobutane dehydrogenation reaction:

$$\text{Isobutane conversion(\%)} = \frac{\text{Isobutane}_{in} - \text{Isobutane}_{out}}{\text{Isobutane}_{in}} * 100 \quad (11)$$

Where  $\text{Isobutane}_{in}$  is the isobutane molar feed flow rate and  $\text{Isobutane}_{out}$  is the isobutane flow rate from outlet of the reaction side.

$$\text{Hydrogen recovery(\%)} = \frac{H_{2,permeate}}{H_{2,permeate} + H_{2,retentate}} * 100 \quad (12)$$

where  $H_{2,permeate}$  is the hydrogen molar flow rate that permeates through the silica membrane,  $H_{2,retentate}$  the hydrogen molar flow rate in retentate side. It should be noted that the Eq.(12) is related to the silica MRs simulation [16].



### 3. Results and discussion

#### 3.1. Model validation

The experimental values of the isobutane conversion obtained by Dangwal et al. [17] were compared with the simulated results for various reaction temperatures; it was verified that the model reproduces quite well the experimental data for the entire range of reaction temperatures. Fig. 2 shows isobutane conversion versus the reaction temperature for the PBR. A comparison between CFD numerical and experimental results reveals that the error ranges between 1 and 3%. These deviations are probably owing to the assumptions given for the CFD model.

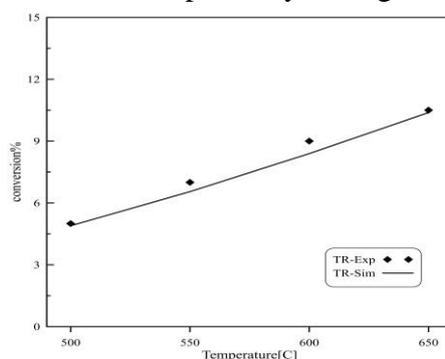


Fig. 2. Comparison of CFD model results and experimental data for PBR (Experimental data by Dangwal et al. [17]).

#### 3.2. Component composition and velocity distribution

Mole fraction distribution of H<sub>2</sub> and isobutane in the both sides of MR is the most important parameters for optimization of process. As illustrated in Fig. 3, during isobutane dehydrogenation reaction for feed flow rate of 8 mol/m<sup>3</sup>, sweep gas flow rate of 1 mol/m<sup>3</sup>, Weight hourly space velocity (WHSV) of 1.37 [1/h], feed pressure 1 bar and reaction temperature 500 C, mole fraction contours H<sub>2</sub> and isobutane determines hydrogen production and isobutane consumption along reaction side, and also removing H<sub>2</sub> from retentate side, simultaneously.

As it is seen, the H<sub>2</sub> is transferred toward the silica membrane due to concentration gradient in radial direction with sweep gas stream. The mass transfer flux in the shell and tube sides is composed of diffusion and convection. The convection mechanism tends to transfer H<sub>2</sub> to the outlet of MR owing to high contribution of velocity in the vertical direction. The H<sub>2</sub> is transferred toward the membrane by diffusional mass transfer that is responsible for H<sub>2</sub> removal.

the velocity magnitudes, as illustrated in Fig. 4, velocity distributions follows a parabolic form in both sides of the dense silica MR. Indeed, the maximum values of velocity is observed in the central area of permeate and retentate sides.

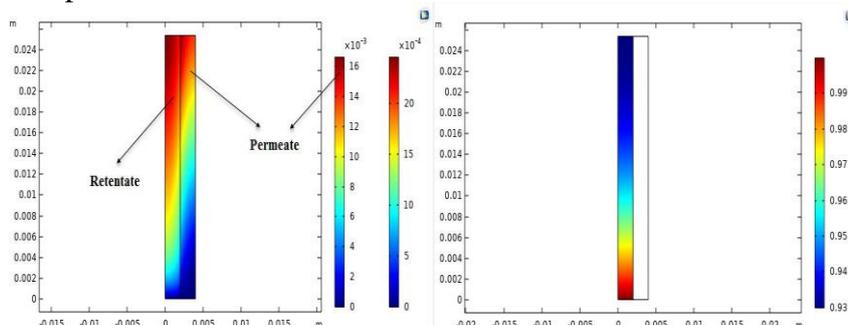


Fig. 3. Mole fraction distribution of (left): H<sub>2</sub> and (Right): isobutane achieved by CFD simulation during isobutane dehydrogenation reaction in silica MR.

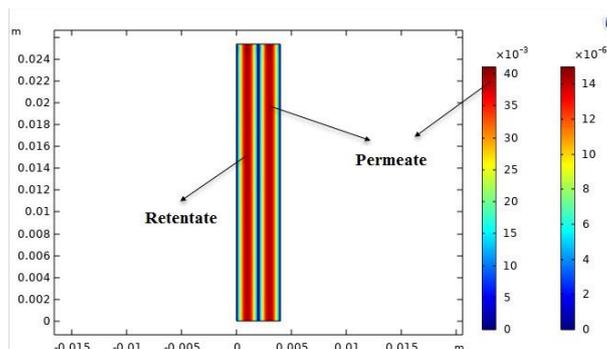
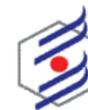


Fig. 4. velocity distribution (m/s) achieved by CFD simulation during isobutane dehydrogenation reaction in silica MR

### 3.3. Effect of operating parameters

#### 3.3.1. Reaction pressure effect

In this section, the simulation was carried out maintaining the reaction temperature equal to 500 C , feed flow rate of 8 mol/m<sup>3</sup>, sweep gas flow rate of 1 mol/m<sup>3</sup>, feed velocity of WHSV=1.37[1/h] for cases of silica MRs and TR, in which the reaction pressure has been varied between 1 and 4 atm. Fig. 5 shows isobutane conversion and hydrogen recovery for MR and PBR versus reaction pressure As a general consideration, an increase of reaction pressure in the membrane module can result in competitive effects on isobutane conversion in the silica MR:

- A positive effect, well known as shift effect. In fact, a higher pressure increases the hydrogen partial pressure on the reaction side, resulting in a higher hydrogen flux permeated through the membrane that favors the shift of the isobutane dehydrogenation reaction toward the products, allowing a higher isobutane conversion to be reached.
- A negative consequence due to the thermodynamic limitation of the isobutane dehydrogenation reaction (thermodynamic effect), which proceeds with an enhancement of the mole number, so the reaction is not favored by high pressures.

As the pressure increases, the driving force increases. Subsequently, hydrogen recovery increases.

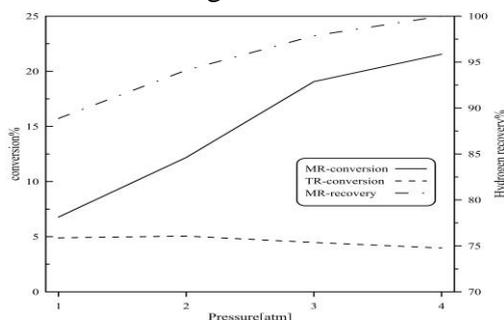
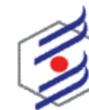


Fig. 5. Effect of reaction pressure on isobutane conversion and hydrogen recovery for silica MR and PBR

Fig. 5 shows that, by increasing the pressure from 1.0 to 4.0 atm, the isobutane conversion enhances for MR while this trend is completely different for case of FBR. This is probably due to the fact that the "shift effect" is prevalent with respect to "thermodynamic effect" on the MR case, but for case of PBR, thermodynamic effect is dominant.

#### 3.3.2. Reaction temperature effect

In this section, the simulation was carried out maintaining the reaction pressure equal to 1 bar, feed flow rate of 8 mol/m<sup>3</sup>, sweep gas flow rate of 1 mol/m<sup>3</sup>, WHSV=1.37[1/h] for cases of silica MRs and PBR, in which the reaction temperature has been varied between 500 and 650 C. Fig. 6 shows isobutane conversion for MR and PBR and hydrogen recovery for MR versus



reaction temperature. For each case, regarding to endothermic nature of the isobutane dehydrogenation reaction system, the isobutane conversion should be increased, that this trend was confirmed that CFD results. As indicated in Fig. 6, the isobutane conversion achieved in the MR may overcome the thermodynamic equilibrium conversion related to PBR. At higher temperatures, owing to the H<sub>2</sub> permeance mechanism in the silica membrane, the H<sub>2</sub> flux is much higher, so isobutane conversion enhancement for case of silica MR with respect to PBR is higher than once obtained in lower temperatures.

Meanwhile, Fig. 6 displays hydrogen recovery versus reaction temperature for silica MR. The hydrogen recovery is improved by increasing the reaction temperature in both cases. In fact, by considering permeation equation (Eq. (7)), a higher reaction temperature results in a higher hydrogen permeation flux involving a higher hydrogen stream recovered in the permeate side.

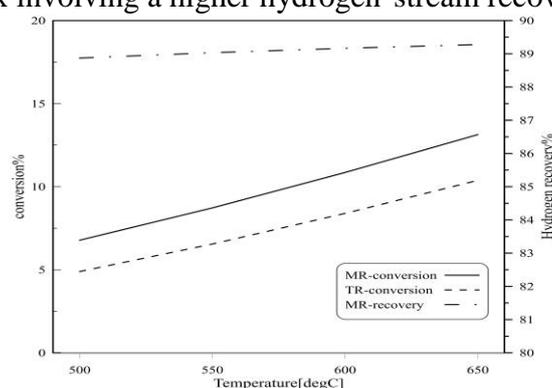


Fig. 6. Effect of reaction temperature on isobutane conversion and hydrogen recovery silica MR and PBR

#### 4. Conclusions

In this work, the isobutane dehydrogenation reaction in a dense silica MR was evaluated for hydrogen production from CFD point of view. To this purpose, a 2D, isothermal model was developed using CFD method for evaluation of dense silica MR performance during isobutane dehydrogenation reaction. A good agreement was achieved between CFD modeling results and literatures experimental data. After model validation, this study was focused on the analysis of the isobutane conversion and hydrogen recovery reachable in silica MR with respect to PBR by varying several operating parameters, such as reaction temperature and reaction pressure value. It can be concluded that the isobutane conversion realized in silica is higher than the ones achieved for PBR during isobutane dehydrogenation reaction, in all studied cases. In general, regarding to CFD results, a reasonable enhancement of isobutane conversion by silica MR at high reaction pressures and low temperatures can be achievable. As a consequence, by improving silica membrane structure and achieving higher permeance, the silica MR can be used for various applications in the future, without commercializing and economic challenges.

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