Reduction in CO emissions along a two-stage hydrogen-permselective membrane reactor in methanol synthesis process

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1. Introduction

Carbon monoxide (CO) is a scentless and invisible gas that is quite poisonous. It is also known to be a major environmental pollutant. Industrial chemical processes contribute to CO pollution levels in the atmosphere. One of the most important processes for controlling the carbon monoxide content is conversion of CO to methanol by catalytic hydrogenation. The present work investigates enhancement of CO conversion in a conventional two-stage methanol synthesis reactor using a hydrogen-permselective membrane. For this membrane system, a one-dimensional dynamic plug flow model was proposed in the presence of long-term catalyst deactivation. This model compares CO removal in a membrane two-stage methanol synthesis reactor with a conventional two-stage methanol synthesis reactor. A conventional two-stage reactor is a vertical shell and tube in which the first reactor coolant is saturated water and the second one is cooled with synthesis gas. In a membrane two-stage reactor, the wall of the tubes in the gas-cooled reactor is coated with a Pd–Ag membrane, which only permits the diffusion of hydrogen. For validation of the recommended dynamic model, the measured daily process data of a methanol plant recorded for a period of 4 years were used and a good agreement was obtained.

low expense, simple to storage and eminent miscibility with water. Hydrogen plays a major role in the future as a carbon-free fuel for installing H2 reforming unit to a portable fuel cell, compact design of reformer is mainly the strategic point [3–6]. Commercially, methanol can be recovered from many resources and is produced by catalytic conversion of synthesis gas in large scale. Synthesis gas consists of CO, CO2, and H2 and some inert components like CH4 and N2.

At the entrance of the methanol reactor, the reactions are rate base, so increasing temperature enhances rate of reaction and CO conversion, but at the end of reactor, the reactions are equilibrium base and increasing temperature, decreases CO equilibrium conversion. Therefore, in order to reach the highest removal rate of CO, implementing a higher temperature at the entrance of the reactor and then reducing temperature gradually towards the exit of reactor is one of the significant issues in methanol synthesis reactor.

Recently, a two-stage methanol synthesis reactor was introduced by Lurgi instead of a single-type for CO conversion to methanol [7]. This system is an advanced technology for converting synthesis gas to methanol at low cost and in large quantities. The configuration of this system is based on the two-stage reactor system. The first is a high temperature water-cooled reactor that is combined in series with a low temperature gas-cooled reactor and partial conversion of CO to methanol is
accomplished in this reactor. Reacting gas composition in the second reactor is essentially poor in H₂, so performance of this reactor is lower than first reactor and decreases system efficiency. One way to reach higher conversion of CO to methanol is the addition of hydrogen to the reacting gas selectively by using membrane in gas-cooled reactor that leads to a shift of the chemical equilibrium towards the product side [8].

A membrane two-stage methanol synthesis reactor is a modified system which combines the chemical and membrane conversion in one system [9]. The main advantages of this system are: enhancement of CO conversion, overcoming with the potential limitations imposed by thermodynamic equilibrium [8], improvement of kinetics-limited reactions in the first reactor due to the higher feed temperature, enhancement of equilibrium limited reactions due to a lower temperature in the gas-cooled reactor and control of stoichiometric number of reacting gases along the second reactor by hydrogen diffusion through the membrane. The membrane separation is governed by both the chemical nature of the membrane material and the physical structure of the membrane [10]. Membrane conversion technology in chemical reaction processes is mainly used in reaction systems containing hydrogen and oxygen, and is based on inorganic membranes [11]. It was observed that diffusion of hydrogen through palladium membranes can enhance the selectivity of hydrogenation [12]. The use of Pd membranes is hindered because palladium shows a transition from the α-phase (hydrogen poor) to the β-phase (hydrogen rich) at temperatures below 300 °C and pressures below 2 MPa, depending on the hydrogen concentration in the metal. Since the lattice constant of the α-phase is 3% smaller than that of the β-phase this transition leads to lattice strain, and consequently after a few cycles, to a deformity of the metal lattice [13]. In many hydrogen-related reaction systems, Pd-alloy membranes on a stainless steel support were used as the hydrogen-permeable membrane [14]. A maximum value of hydrogen permeability is reached for an alloy with composition of 23 wt% silver [15].

For decades, palladium-based membranes have been used in transport of hydrogen because of their high permeability, good surface properties and 100% hydrogen selectivity [16]. These membranes combine hydrogen transition with distinguishing properties such as resistance to high temperatures, solvents, and corrosion. The main cause of the Pd-based membranes development is: low costs as well as perm-selectivity combined with good mechanical, thermal and long-term stability [17]. These properties make interesting use of palladium-based membranes such as Pd–Ag membranes in petrochemical industry.

There is one study on conversion of CO to methanol in Pd–Ag membrane single-type methanol synthesis reactor [8], but no investigation regarding the use of a Pd-membrane in two-stage methanol synthesis reactor for enhancement of CO conversion. Therefore, it was decided to first study on this system.

The aim of present work is reduction of carbon monoxide emission in a conventional two-stage methanol synthesis reactor. In this system, the walls of tubes in the gas-cooled reactor are covered with a layer of hydrogen perm-selective membrane. The driving force for hydrogen diffusion is its partial pressure gradient from feed synthesis gas to the reacting gas. The advantages of this concept will be discussed based on temperature, activity of catalyst and concentration profiles. The results are compared with the performance of conventional two-stage methanol synthesis reactor.

2. Process description

2.1. Conventional two-stage methanol synthesis reactor

Schematic diagram of a conventional two-stage methanol synthesis reactor is shown in Fig. 1.

The catalyst is packed in shell side of water-cooled reactor and vertical tubes of gas-cooled reactor. Reactions of methanol synthesis are performed over commercial CuO/ZnO/Al₂O₃ catalyst. Cold feed synthesis gas is fed to tubes of the second reactor and is flowing in counter-current mode with methanol-containing reacting gas in the shell of this reactor. Then outlet synthesis gas is entered to tubes of the first reactor and chemical reaction initiated by catalyst. The remaining heat of reaction is transferred to the cooling water inside the shell. In this stage, CO is partly converted to methanol. Then reacting gas mixture is left directing to the catalyst shell side of second reactor and its temperature is continuously reduced through the catalyst bed. Finally, the product is removed from the side stream of second reactor.

Temperature of the first reactor is higher than second reactor so the main catalyst deactivation occurs in this reactor. Therefore, the lower operating temperature in the gas-cooled reactor results in a practically unlimited catalyst service life. In addition, reaction control extends catalyst life time of the water-cooled reactor.

Fig. 1. Schematic flow diagram of conventional two-stage methanol synthesis reactor.
The input data and industrial design of the catalyst pellet for the conventional two-stage methanol synthesis reactor have been listed in Tables 1 and 2.

2.2. Membrane two-stage methanol synthesis reactor

Fig. 2 shows the schematic diagram of a membrane two-stage methanol synthesis reactor configuration for CO conversion.

Procedure of membrane system is similar to conventional two-stage methanol synthesis reactor, with the exception that in this system, the walls of tubes in the gas-cooled reactor are coated with a hydrogen perm-selective membrane. The pressure difference between the shell (71.2 bar) and tubes (76.98 bar) permits the hydrogen diffusion through the Pd–Ag membrane layer. On the other hand, in the new system, mass and heat transfer process simultaneously occurs between the shell and tube, while in the conventional-type only a heat transfer process occurs between them.

The membrane specifications are listed in Table 3. Also, all specifications for the membrane two-stage system in the first and second methanol synthesis reactors are the same as of the conventional methanol synthesis reactor summarized in Tables 1 and 2.

3. Mathematical model

The mathematical model for the simulation of membrane two-stage methanol synthesis reactor was developed based on the following assumptions:

(1) One-dimensional plug flow;
(2) Axial dispersion of heat is negligible compared with convection;
(3) Gases are ideal;
(4) Radial diffusion in the catalyst pellet is neglected;
(5) There are no radial concentration and temperature gradients;
(6) The axial diffusion of hydrogen through the membrane is neglected compared to the radial diffusion;

In Fig. 3 an elemental of length $\Delta z$ is considered.

3.1. Water-cooled reactor

In tube side mass and energy balance for solid phase are expressed by:

$$v_s \frac{\partial y_{su}^o}{\partial t} = \frac{S}{r_\text{c}} \left( v_{\text{in}} y_{\text{in}} - y_{\text{su}}^o \right) + \eta_r \rho_l a_i, \quad i = 1, 2, \ldots, N - 1$$

(1)

$$\rho_l c_p \frac{\partial T_{su}^o}{\partial t} = a_h \left( T_{\text{in}} - T_{su}^o \right) + \rho_l a \sum_{i=1}^{N} \eta_r (\Delta H_{f,i})$$

(2)

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Water-cooled reactor</th>
<th>Gas-cooled reactor</th>
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<tbody>
<tr>
<td>$D$</td>
<td>4.5</td>
<td>5.5</td>
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<tr>
<td>$D_1$</td>
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<tr>
<td>$D_0$</td>
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<tr>
<td>$d_p$</td>
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<td>$\rho_l$</td>
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<td>1770</td>
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<tr>
<td>$c_p$</td>
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<td>5.0</td>
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<tr>
<td>$\lambda_c$</td>
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<td>$\omega$</td>
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<tr>
<td>$e_{s}$</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>Tube length</td>
<td>8</td>
<td>10</td>
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<tr>
<td>Number of tubes</td>
<td>5955</td>
<td>3026</td>
</tr>
<tr>
<td>Shell side pressure</td>
<td>–</td>
<td>71.2</td>
</tr>
<tr>
<td>Tube side pressure</td>
<td>75</td>
<td>76.98</td>
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Table 2

<table>
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<th>Feed conditions</th>
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<td>Feed composition (mol%)</td>
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<td>CO</td>
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<td>CO$_2$</td>
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</tr>
<tr>
<td>H$_2$</td>
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</tr>
<tr>
<td>CH$_4$</td>
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</tr>
<tr>
<td>N$_2$</td>
<td>8.2</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.1</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>0.37</td>
</tr>
<tr>
<td>Argon</td>
<td>0.24</td>
</tr>
<tr>
<td>Inlet temperature (K)</td>
<td>401</td>
</tr>
<tr>
<td>Total molar flow rate per tube (mol s$^{-1}$)</td>
<td>7.1</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>76</td>
</tr>
</tbody>
</table>

Fig. 2. Schematic flow diagram of membrane two-stage methanol synthesis reactor.
where \( y_{it}^{u} \) and \( T_{it}^{u} \) are the mole fraction and temperature of solid-phase in tube side, respectively, and \( i \) represents \( \text{CH}_3\text{OH}, \text{CO}, \text{CO}_2, \text{H}_2, \text{H}_2\text{O} \). Argon, nitrogen and methane are inert components. The following two conservation equations are written for the fluid phase:

\[
\frac{\partial y_{it}^{u}}{\partial t} = - \frac{1}{A_{it}^{u}} \frac{\partial F_{it}^{u}}{\partial z} + a_t c_t k_{tp}(y_{it}^{u} - y_{it}^{\text{ph}}), \quad i = 1, 2, \ldots, N - 1
\]  
(3)

\[
\frac{\partial p_{it}^{\text{ph}}}{\partial t} = - \frac{1}{A_{it}^{\text{ph}}} \frac{\partial F_{it}^{\text{ph}}}{\partial z} + a_t \Delta h_f(T_{it}^{\text{ph}} - T_{it}^{u}) + \frac{\alpha_{it}^{\text{ph}}}{A_{it}^{\text{ph}}} (\sqrt{p_{it}^{\text{ph}}} - \sqrt{p_{it}^{\text{ph}}})
\]  
(4)

where \( y_{it}^{u} \) and \( T_{it}^{u} \) are the fluid-phase mole fraction and temperature in tube side, respectively, and \( F_{it}^{u} \) and \( A_{it} \) are total molar flow rate and cross-section in each tube, respectively. The boundary conditions are unknown and the more details are clarified in numerical solution.

\[ z = 0: \quad F_{it} = F, \quad y_{it}^{u} = y_{it}^{\text{in}}, \quad T_{it}^{u} = T_{in} \]  
(5)

The initial conditions are:

\[ t = 0: \quad y_{it}^{u} = y_{it}^{\text{in}}, \quad y_{it}^{\text{ph}} = y_{it}^{\text{ph} \text{in}}, \quad T_{it}^{u} = T_{in}, \quad T_{it}^{\text{ph}} = T_{in}, \quad a = 1 \]  
(6)

3.2. Gas-cooled reactor

3.2.1. Shell side

Overall mass balance:

\[
\frac{\partial c_t}{\partial t} = - \frac{1}{A_{it}^{u}} \frac{\partial F_{it}^{u}}{\partial z} + \alpha_{it}^{u} (\sqrt{p_{it}^{u}} - \sqrt{p_{it}^{u}})
\]  
(7)

where \( c_t, F_{it}^{u} \) are total concentration and flow rate of reacting gas mixture in shell side. \( A_{it}^{u} \) is cross-sectional area of shell and \( \alpha_{it}^{u} \) is rating constant of hydrogen permeation. \( p_{it}^{u} \) and \( p_{it}^{u} \) are partial pressure of hydrogen in tube and shell sides, respectively. The mass and energy balance in the gas-cooled reactor for solid phase are the same as water-cooled reactor. The following equations are written for fluid phase:

\[
\frac{\partial y_{it}^{ph}}{\partial t} = - \frac{1}{A_{it}^{ph}} \frac{\partial F_{it}^{ph}}{\partial z} + a_t c_t k_{tp}(y_{it}^{u} - y_{it}^{ph}) + \frac{\alpha_{it}^{ph}}{A_{it}^{ph}} (\sqrt{p_{it}^{ph}})
\]  
(8)

where \( y_{it}^{ph} \) and \( T_{it}^{ph} \) are the mole fraction and temperature of solid phase in shell side, respectively.

\[ \text{Nomenclature:} \]

\begin{align*}
\alpha_{it}^{u} & : \text{rating constant of hydrogen permeation} \\
A_{it}^{u} & : \text{cross-sectional area of shell} \\
A_{it}^{ph} & : \text{cross-sectional area of shell} \end{align*}

3.2.2. Tube side

Overall mass balance:

\[
\frac{\partial c_t}{\partial t} = - \frac{1}{A_{it}^{u}} \frac{\partial F_{it}^{u}}{\partial z} - \alpha_{it}^{ph} (\sqrt{p_{it}^{ph}} - \sqrt{p_{it}^{ph}})
\]  
(12)

where \( c_t, F_{it}^{u} \) are total concentration and flow rate in tube side. The mass and energy balance equations for fluid phase are given:

\[
\frac{\partial y_{it}^{ph}}{\partial t} = - \frac{1}{A_{it}^{ph}} \frac{\partial F_{it}^{ph}}{\partial z} + \alpha_{it}^{ph} (\sqrt{p_{it}^{ph}} - \sqrt{p_{it}^{ph}}), \quad i = 1, 2, \ldots, N - 1
\]  
(13)

\[
\frac{\partial p_{it}^{ph}}{\partial t} = - \frac{1}{A_{it}^{ph}} \frac{\partial F_{it}^{ph}}{\partial z} + \alpha_{it}^{ph} (\sqrt{p_{it}^{ph}} - \sqrt{p_{it}^{ph}}) + \frac{\alpha_{it}^{ph}}{A_{it}^{ph}} (\sqrt{p_{it}^{ph}} - \sqrt{p_{it}^{ph}}) \times (\sqrt{p_{it}^{ph}} - \sqrt{p_{it}^{ph}})
\]  
(14)

The boundary conditions are as follow:

\[ z = L: \quad y_{it}^{ph} = y_{it}^{f}, \quad T_{it}^{ph} = T_{f} \]  
(15)

when \( \alpha_{it}^{u} = 0 \), the membrane is not permeable to hydrogen and the model is used for industrial two-stage system.

3.3. Deactivation model

The deactivation model of the CuO/ZnO/Al2O3 catalyst has been studied by several researchers, however, the suggested model by Hanken was found to be suitable for industrial applications [18]:

\[
\exp \left( \frac{-E_d}{R} \left( \frac{1}{T} - \frac{1}{T_R} \right) \right) \alpha_{t}^{u} C_{m} \frac{d\alpha_{t}^{u}}{dt} = -K_d
\]  
(16)

where \( E_d, T_R \) and \( K_d \) are the activation energy, reference temperature and catalyst deactivation constant, respectively. These parameters are listed in Table 4 [18]. The above model has been fitted with industrial operating conditions and is the only case for simulation and modeling of industrial plants.

Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_d )</td>
<td>0.00439</td>
<td>[h⁻¹]</td>
</tr>
<tr>
<td>( E_d )</td>
<td>91.270</td>
<td>[kJ mol⁻¹]</td>
</tr>
<tr>
<td>( T_R )</td>
<td>513</td>
<td>[K]</td>
</tr>
</tbody>
</table>

![Fig. 3. Schematic diagram of an elemental volume of the second reactor in membrane two-stage system.](image-url)
3.4. Hydrogen permeation in the Pd/Ag membrane

The flux of hydrogen permeating through the palladium membrane ($j_H$) depends on the difference in the hydrogen partial pressure on the two sides of the membrane. Here, the hydrogen permeation is determined assuming Sieverts’ law:

$$j_H = \alpha_H \left( P_{\text{H}_2} - P_{\text{H}_2}^0 \right)$$

where $\alpha_H$ is the hydrogen permeation rate constant and is defined as [19]:

$$\alpha_H = \frac{2\pi L P_0}{\ln(R_o/R_i)}$$

where $R_o$, $R_i$ are the outer and inner radius of the Pd/Ag layer.

4. Numerical solution

The fundamental structure of the model is consisted of the partial derivative equations of mass and energy conservative rules of both the solid and fluid phase, which have to be coupled with the ordinary differential equation of the deactivation model, and also non-linear algebraic equations of the kinetic model and auxiliary correlations. The equations are solved using a two-stage approach consisting of a steady-state simulation stage followed by a dynamic simulation stage. In order to solve the set of reactor model equations, a steady-state simulation has been used prior to a dynamic simulation and gives the initial values of the dynamic one.

4.1. Steady-state model solution

Steady-state model solution of the two-stage methanol reactor is carried out by setting all the time-variation of the states to zero at time zero ($t = 0$). According to Eq. (16) catalyst activity is a function of temperature as follows [20,21]:

$$\alpha_H = \frac{2\pi L P_0}{\ln(R_o/R_i)}$$

where the pre-exponential factor $P_0$ above 200 °C is reported as $6.33 \times 10^{-4} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1/2}$ and activation energy $E_p$ is $15.7 \text{ kJ mol}^{-1}$ [20,21].

5. Model validation

5.1. Steady-state model validation

The steady-state model was validated by comparing its results at time zero ($t = 0$) with plant data for a conventional two-stage methanol synthesis reactor ($\alpha_H \approx 0$) under the design specifications. Input data presented in Tables 1 and 2, respectively. The model results and data of the plant are tabulated in Table 5. It was observed that the steady-state model carried out acceptably well under industrial conditions and result of simulation with daily-real plant data were a good agreement.

5.2. Dynamic model validation

In order to verify the goodness of dynamic model, simulation results have been compared with the historical process data for single-stage reactor. The predicted results of production rate and the corresponding observed data of the plant are presented in Table 6. It was observed that, the model performed satisfactorily well under industrial conditions and a good agreement between daily-observed plant data and simulation data existed.

6. Results and discussion

A parametric analysis is performed to address the vital issues, such as the catalyst activity, temperature, CO mole fraction and removal rate profiles along the reactors. Fig. 4 shows a comparison of catalyst activity and temperature profiles, CO mole fraction and CO removal rate profiles along the conventional and membrane two-stage methanol synthesis reactor at 1st and 1400th days of operation. According to Eq. (16) catalyst activity is a function of temperature, thus local variation of temperature along the reactor causes local change in catalyst activity. As seen in parts (a and b),

**Table 5**

<table>
<thead>
<tr>
<th>Composition (mol%)</th>
<th>Plant</th>
<th>Predicted</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OH</td>
<td>0.104</td>
<td>0.1023</td>
<td>-3.4</td>
</tr>
<tr>
<td>CO</td>
<td>0.0251</td>
<td>0.0228</td>
<td>-4.38</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.0709</td>
<td>0.0764</td>
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</tr>
<tr>
<td>H$_2$O</td>
<td>0.0234</td>
<td>0.0211</td>
<td>-9.82</td>
</tr>
<tr>
<td>H$_2$</td>
<td>0.5519</td>
<td>0.5323</td>
<td>-3.55</td>
</tr>
<tr>
<td>N$_2$/Ar</td>
<td>0.9968</td>
<td>0.9905</td>
<td>-6.5</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>0.114</td>
<td>0.103</td>
<td>-9.64</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>495</td>
<td>489.5</td>
<td>-1.2</td>
</tr>
<tr>
<td>CO removal rate (tons/day)</td>
<td>4465</td>
<td>4542.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>
the minimum activity level is observed near the entrance of first reactor that is exposed to higher temperature at all times. Also, the temperature profile in the water-cooled reactor of membrane system is higher than conventional up to 8 m in length because the feed synthesis gas in this reactor has a higher temperature than the reacting gas mixture in the gas-cooled reactor. These parts also demonstrate that the second reactor of membrane system due to addition of hydrogen to the reacting materials has a lower temperature. Therefore, the temperature profile along the membrane two-stage reactor is more desirable than the conventional reactor. This desired lower temperature improves both the catalyst activity and equilibrium constant which results in a shift of the equilibrium conversion to a higher value. The favorable thermodynamic equilibrium at lower temperatures and H2 permeation along the membrane two-stage methanol reactor are the main reasons for obtaining the higher CO removal rate in comparison with the conventional system at any time of operation as shown in parts (c) and (d).

Fig. 5(a and b) demonstrates CO mole fraction and CO removal rate versus length and time for membrane two-stage methanol reactor. CO mole fraction decreases along the reactor and increases with time. Catalyst deactivation is the major reason for increase in CO mole fraction and reduction in CO removal rate as time passes. Fig. 6 shows that the catalyst deactivation in the membrane reactor due to lower temperature is less than in the conventional two-stage reactor.

Fig. 7 illustrates CO mole fraction and CO removal rate profiles along the membrane two-stage methanol synthesis reactor at three different times of operation. Between the 1st and 1400th days of operation, catalyst deactivation leads to a conversion reduction. It is shown in this figure that, mole fraction of CO in product stream increases and CO removal rate decreases as times passes.

Fig. 8 shows the CO mole fraction and CO removal rate over a period of 1400 operating days for both types of methanol synthesis reactor systems. As can be seen, there is a considerable increase in amount of CO removal rate in membrane two-stage reactor.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Plant (tons/day)</th>
<th>Predicted (tons/day)</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>295.0</td>
<td>308.80</td>
<td>2.93</td>
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<tr>
<td>100</td>
<td>296.5</td>
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<td>200</td>
<td>302.6</td>
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<td>500</td>
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<td>1200</td>
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<td>255.18</td>
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**Table 6**
Comparison between predicted methanol production rate and plant data.

![Fig. 4](image-url). Comparison of (a and b) catalyst activity and temperature profiles and (c and d) CO mole fraction and CO removal rate profiles along the conventional and membrane two-stage methanol synthesis reactors for 1st and 1400th days of operation.
Carbon monoxide is the most abundant and widely distributed air pollutant. The catalytic hydrogenation of CO to methanol represents an effective method for reducing the harmful effects of this poisonous gas. In this work, a Pd–Ag membrane was used in the second reactor of a two-stage methanol synthesis reactor for enhancement of CO removal and its performance was compared with a conventional two-stage methanol synthesis reactor. Potential possibilities of the membrane were examined using one-dimensional heterogeneous model to obtain the necessary comparative estimates. A comparison of the catalyst temperature profiles along the length of the reactor in both systems shows that in the membrane system, temperature profile of the catalyst bed is very desirable. This advantage leads to:

- Longer catalyst lifetime due to higher activity along the reactor.
- High level of catalyst activity in the gas-cooled reactor results in a higher CO conversion which means higher CO removal rate.

The results of this study show that the application of membrane two-stage methanol synthesis reactor is an attractive system for improvement of CO conversion to methanol and reducing CO emissions into the atmosphere.

Acknowledgement

The authors would like to thank Zagross Petrochemical Company of Iran for providing valuable operating data.
Appendix A. Reaction kinetics

A.1. Reaction kinetics

In the methanol synthesis, three overall reactions are possible: hydrogenation of carbon monoxide, hydrogenation of carbon dioxide and reverse water–gas shift reaction, which follow as:

\[
\begin{align*}
\text{CO} + 2\text{H}_2 &\rightarrow \text{CH}_3\text{OH}, \quad \Delta H_{298} = -90.55 \text{ kJ mol}^{-1} \quad (A.1) \\
\text{CO}_2 + \text{H}_2 &\rightarrow \text{CO} + \text{H}_2\text{O}, \quad \Delta H_{298} = +41.12 \text{ kJ mol}^{-1} \quad (A.2) \\
\text{CO}_2 + 3\text{H}_2 &\rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}, \quad \Delta H_{298} = -49.43 \text{ kJ mol}^{-1} \quad (A.3)
\end{align*}
\]

Reactions (A.1)–(A.3) are not independent so that one is a linear combination of the other ones. In the current work, the rate expressions have been selected from Graaf et al. [22]. The rate equations combined with the equilibrium rate constants [23] provide enough information about kinetics of methanol synthesis. The correspondent rate expressions due to the hydrogenation of CO, CO\textsubscript{2} and the reversed water–gas shift reactions are:

\[
\begin{align*}
& r_1 = \frac{k_1K_{\text{CO}}[f_{\text{CO}}]^{3/2} - f_{\text{CH}_3\text{OH}}/[f_{\text{CO}}]^{1/2}K_{\text{H}_2\text{O}}]}{(1 + K_{\text{CO}}[f_{\text{CO}} + K_{\text{CO}_2}[f_{\text{CO}_2}]^{1/2} + (K_{\text{H}_2\text{O}}/K_{\text{H}_2\text{O}})^{1/2}f_{\text{H}_2\text{O}}]} \quad (A.4) \\
& r_2 = \frac{k_2K_{\text{CO}_2}[f_{\text{CO}_2}]^{3/2} - f_{\text{H}_2\text{O}}/[f_{\text{CO}_2}]^{1/2}K_{\text{H}_2\text{O}}]}{(1 + K_{\text{CO}_2}[f_{\text{CO}_2} + K_{\text{CO}_2}[f_{\text{CO}_2}]^{1/2} + (K_{\text{H}_2\text{O}}/K_{\text{H}_2\text{O}})^{1/2}f_{\text{H}_2\text{O}}]} \quad (A.5) \\
& r_3 = \frac{k_3K_{\text{CO}_2}[f_{\text{CO}_2}]^{3/2} - f_{\text{CH}_3\text{OH}}/[f_{\text{CO}_2}]^{1/2}K_{\text{H}_2\text{O}}]}{(1 + K_{\text{CO}_2}[f_{\text{CO}_2} + K_{\text{CO}_2}[f_{\text{CO}_2}]^{1/2} + (K_{\text{H}_2\text{O}}/K_{\text{H}_2\text{O}})^{1/2}f_{\text{H}_2\text{O}}]} \quad (A.6)
\end{align*}
\]

The reaction rate constants, adsorption equilibrium constants and reaction equilibrium constants which occur in the formulation of kinetic expressions are tabulated in Tables A.1–A.3, respectively.

### Table A.1

<table>
<thead>
<tr>
<th>Reaction rate constants [22].</th>
<th>A (\times 10^7)</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(k_1)</td>
<td>(4.89 ± 0.29)</td>
<td>-113,000 ± 300</td>
</tr>
<tr>
<td>(k_2)</td>
<td>(9.64 ± 7.30)</td>
<td>-152,900 ± 11,800</td>
</tr>
<tr>
<td>(k_3)</td>
<td>(1.09 ± 0.07)</td>
<td>-87,500 ± 300</td>
</tr>
</tbody>
</table>

### Table A.2

<table>
<thead>
<tr>
<th>Adsorption equilibrium constants [22].</th>
<th>A (\times 10^{-5})</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{\text{CO}})</td>
<td>(2.16 ± 0.44)</td>
<td>46,800 ± 800</td>
</tr>
<tr>
<td>(K_{\text{CO}_2})</td>
<td>(7.05 ± 1.39)</td>
<td>61,700 ± 800</td>
</tr>
<tr>
<td>((K_{\text{H}<em>2\text{O}}/K</em>{\text{H}_2\text{O}})^{1/2})</td>
<td>(6.37 ± 2.88)</td>
<td>84,000 ± 1400</td>
</tr>
</tbody>
</table>

### Table A.3

<table>
<thead>
<tr>
<th>Reaction equilibrium constants [22].</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(K_{\text{H}_2\text{O}})</td>
<td>5139</td>
<td>12,621</td>
</tr>
<tr>
<td>(K_{\text{CO}_2})</td>
<td>-2073</td>
<td>-2,029</td>
</tr>
<tr>
<td>(K_{\text{CO}_2})</td>
<td>3066</td>
<td>10,592</td>
</tr>
</tbody>
</table>

Appendix B. Auxiliary correlations

B.1. Mass transfer correlations

In the current work, mass transfer coefficients for the components have been taken from Cusler [24]. These are mass transfer coefficients between gas phase and solid phase.

\[
k_{gi} = 1.17R e^{-0.42S c_i - 0.67}u_g \times 10^3 \quad (B.1)
\]

where the Reynolds and Schmidt numbers have been defined as:

\[
Re = \frac{2R_p u_g}{\mu} \quad (B.2)
\]

\[
Sc_i = \frac{\mu}{\rho D^{1/2}} \times 10^{-4} \quad (B.3)
\]

And the diffusivity of component \(i\) in the gas mixture is given by [25].

\[
D_{ij} = \frac{10^{-7}p^{3/2}/\sqrt{(1/M_i) + (1/M_j)}}{P(v_i^{3/2} + v_j^{3/2})} \quad (B.5)
\]

Knowing the fact that diffusion path length along the pores is greater than the measurable thickness of the pellet, for the effective diffusivity in the catalyst pore, correction should be implemented due to the structure of the catalyst. The correction factor is ratio of catalyst void fraction to the tortuosity of the catalyst (\(\tau\)).

B.2. Heat transfer correlations

The overall heat transfer coefficient between circulating boiling water of the shell side and bulk of the gas phase in the tube side is given by the following correlation.

\[
\frac{1}{U_{\text{shell}}} = \frac{1}{h_i} + \frac{A_i}{2\pi L K_w} + \frac{A_i}{A_0 h_0} \quad (B.6)
\]

where \(h_i\) is the heat transfer coefficient between the gas phase and reactor wall and is obtained by the following correlation [28].

\[
h_i = \frac{c_p \mu}{k} \left(\frac{c_p \mu}{K}\right)^{2/3} = \frac{0.458}{\varepsilon_g} \left(\frac{\rho d_p}{\mu}\right)^{-0.407} \quad (B.7)
\]

where in the above equation, \(u\) is superficial velocity of gas and the other parameters are those of bulk gas phase and \(d_p\) is the equivalent catalyst diameter, \(K\) is thermal conductivity of gas, \(\rho, \mu\)

### Table B.1

Molecular weight and critical volume of the components.

<table>
<thead>
<tr>
<th>Component</th>
<th>(M_i) (g mol(^{-1}))</th>
<th>(v_{\text{cr}}) ((10^4 \text{m}^3 \text{mol}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{OH})</td>
<td>32.04</td>
<td>118.0</td>
</tr>
<tr>
<td>CO</td>
<td>28.01</td>
<td>18.0</td>
</tr>
<tr>
<td>(\text{CO}_2)</td>
<td>44.01</td>
<td>94.0</td>
</tr>
<tr>
<td>(\text{H}_2\text{O})</td>
<td>18.02</td>
<td>56.0</td>
</tr>
<tr>
<td>(\text{H}_2)</td>
<td>2.02</td>
<td>6.1</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>16.04</td>
<td>99.0</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>28.01</td>
<td>18.5</td>
</tr>
</tbody>
</table>
are density and viscosity of gas, respectively and \( \varepsilon_B \) is void fraction of catalyst bed.

In Eq. (B.6), \( h_w \) is the heat transfer coefficient of boiling water in the shell side which is estimated by the following equation [29]:

\[
h_w = 7.96(T - T_{sat})^3 \left( \frac{P}{P_{sw}} \right)^{0.4} \quad (B.8)
\]

\( T \) and \( P \) are temperature and pressure of boiling water in the shell side, \( T_{sat} \) is the saturated temperature of boiling water at the operating pressure of shell side and \( P_w \) is the atmospheric pressure. The last term of the above equation has been considered due to effect of pressure on the boiling heat transfer coefficient. For the heat transfer coefficient between bulk gas phase and solid phase \( h_f \), Eq. (B.7) is applicable.

**Appendix C. Nomenclature**

**Greek letters**

- \( \alpha_H \) hydrogen permeation rate constant \((\text{mol m}^{-1} \text{s}^{-1} \text{Pa}^{-1/2})\)
- \( \Delta H_{f,i} \) enthalpy of formation of component \( i \) \((\text{J mol}^{-1})\)
- \( \Delta H_{298,i} \) enthalpy of reaction at 298 K \((\text{J mol}^{-1})\)
- \( \varepsilon_B \) void fraction of catalyst bed
- \( \varepsilon_c \) void fraction of catalyst
- \( \mu \) viscosity of fluid phase \((\text{kg m}^{-1} \text{s}^{-1})\)
- \( \nu \) stoichiometric coefficient
- \( \nu_{cr} \) critical volume of component \( i \) \((\text{cm}^3 \text{ mol}^{-1})\)
- \( \rho \) density of fluid phase \((\text{kg m}^{-3})\)
- \( \rho_B \) density of catalyst bed \((\text{kg m}^{-3})\)
- \( \rho_c \) density of catalyst \((\text{kg m}^{-3})\)
- \( \eta \) catalyst effectiveness factor
- \( \tau \) tortuosity of catalyst
- \( \Omega \) auxiliary variable
- \( \Delta \) thickness of membrane \((\text{m})\)

**Superscripts and subscripts**

- \( i \) component \( i \)
- \( f \) feed conditions
- \( p \) permeation side
- \( in \) inlet conditions
- \( out \) outlet conditions
- \( k \) reaction number index (1, 2 or 3)
at catalyst surface
shell side
initial conditions (i.e., steady-state condition)
tube side

References