Comparison of two different flow types on CO removal along a two-stage hydrogen permselective membrane reactor for methanol synthesis

M.R. Rahimpour *, S. Mazinani, B. Vaferi, M.S. Baktash

Chemical Engineering Department, Chemical and Petroleum Engineering School, Shiraz University, Shiraz 71345, Iran

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Abstract
Carbon monoxide (CO) is a gaseous pollutant with adverse effects on human health and the environment. Industrial chemical processes contribute significantly to CO accumulation in the atmosphere. One of the most important processes for controlling carbon monoxide emissions is the conversion of CO to methanol by catalytic hydrogenation. In this study, the effects of two different flow types on the rate of CO removal along a two-stage hydrogen permselective membrane reactor have been investigated. In the first configuration, fresh synthesis gas flows in the tube side of the membrane reactor counter-currently with reacting material in the shell side, so that more hydrogen is provided in the first sections of the reactor. In the second configuration, fresh synthesis gas flows in the tube side of the membrane reactor counter-currently with reacting material in the shell side, so that more hydrogen is provided in the last sections of the reactor. For this membrane system, a one-dimensional dynamic plug flow model in the presence of catalyst deactivation was developed. Comparison between co-current and counter-current configurations shows that the reactor operates with higher conversion of CO and hydrogen permeation rate in the counter-current mode whereas; longer catalyst life is achieved in the co-current configuration. Enhancement of CO removal in the counter-current mode versus the co-current configuration results in an ultimate reduction in CO emissions into the atmosphere.

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1. Introduction

Carbon monoxide (CO) is a poisonous, colorless, and lethal gas which is a byproduct of incomplete combustion of hydrocarbon-based fuels. This gas has a potential health hazard because when breathed it displaces oxygen in the blood and deprives the heart, brain, and other vital organs of oxygen. Once inside the lungs, CO molecules pass easily into the bloodstream and compete with oxygen for hemoglobin in red blood cells. About 95% of the absorbed CO readily binds with hemoglobin to form carboxyhemoglobin (a compound that inhibits the blood’s capacity to carry oxygen to organs and tissues) because the affinity of hemoglobin for CO is over 200 times stronger than it is for oxygen. Thus, the percentage of total hemoglobin in blood that is in the form of carboxyhemoglobin is a biomarker of CO exposure [1,2]. In addition, CO is one of the main reactive trace-gases in the earth’s atmosphere. Reduction in CO concentration can significantly counteract the growth of CH4, so contributes indirectly to global warming and ozone depletion [3–5]. To minimize these effects, carbon monoxide emissions from industrial sources have to be decreased. One possible approach is recycling and fixing CO in a chemical process to form useful products such as methanol that is regarded as an effective method for the reduction of carbon monoxide in the atmosphere. In recent years, a growing interest has been observed in the application of methanol as a green fuel, which can be used directly for powering Otto engines or fuel cells achieving high thermodynamic efficiencies. It can be safely transported by road, rail, barge, ocean tanker or in pipelines. Methanol also contributes significantly to sustainable energy conversion systems as saves a reasonable amount of fossil resources and has almost no impact on the greenhouse effect.

The reforming of natural gas is an industrially established process for the production of methanol [6–9]. It is basically synthesized in three steps: synthesis gas generation, methanol synthesis and methanol distillation. Synthesis gas generation accounts for more than 50% of the capital cost of a methanol plant. Synthesis gas consists of CO, CO2, and H2 and several inert components like CH4 and N2. The main step of methanol process is methanol synthesis. Even though many improvements from its first commercial implementation and a series of new technologies are arising to get it [10], methanol is still largely produced by the natural gas and specifically by means of syngas (CO and H2 mixture) obtained via steam reforming operations.

At the entrance of methanol reactors, the reactions are rate-base, so increasing temperature enhances rate of reaction and CO conversion. At the exit of the reactor, however, the reactions are
CO is a major issue in methanol synthesis. Recently, a two-stage (instead of a single-type) methanol synthesis reactor has been introduced by Lurgi for CO conversion to methanol at low cost and in large quantities. The system basically consists of two reactors. The first

**Nomenclature**

- $A_e$ cross section area of each tube ($m^2$)
- $A_i$ inner area of each tube ($m^2$)
- $A_o$ outside area of each tube ($m^2$)
- $A^{ph}$ cross section area of shell ($m^2$)
- $a$ activity of catalyst
- $a_v$ specific cross section area of shell ($m^2$)
- $c_{ph}$ specific heat of the hydrogen at constant pressure ($J \cdot mol^{-1} \cdot K^{-1}$)
- $c_{ps}$ specific heat of the catalyst at constant pressure ($J \cdot mol^{-1} \cdot K^{-1}$)
- $c_t$ total concentration ($mol \cdot m^{-3}$)
- $D$ reactor diameter ($m$)
- $D_i$ tube inside diameter ($m$)
- $D_{ij}$ binary diffusion coefficient of component $i$ in $j$ ($m^2 \cdot s^{-1}$)
- $D_m$ diffusion coefficient of component $i$ in the mixture ($m^2 \cdot s^{-1}$)
- $D_o$ tube outside diameter ($m$)
- $D_{pi}$ particle diameter ($m$)
- $E_d$ activation energy used in the deactivation model ($J \cdot mol^{-1}$)
- $f_i$ partial fugacity of component $i$ (bar)
- $h_f$ gas-catalyst heat transfer coefficient ($W \cdot m^{-2} \cdot K^{-1}$)
- $h_t$ heat transfer coefficient between fluid phase and reactor wall ($W \cdot m^{-2} \cdot K^{-1}$)
- $h_o$ heat transfer coefficient between coolant stream and reactor wall ($W \cdot m^{-2} \cdot K^{-1}$)
- $K$ conductivity of fluid phase ($W \cdot m^{-1} \cdot K^{-1}$)
- $K_d$ deactivation model parameter constant ($s^{-1}$)
- $K_{pi}$ adsorption equilibrium constant for component $i$ (bar$^{-1}$)
- $K_{eq}$ equilibrium constant based on partial pressure for component $i$ ($-$)
- $K_{ps}$ thermal conductivity of reactor wall ($W \cdot m^{-1} \cdot K^{-1}$)
- $k_1$ reaction rate constant for the 1st rate equation ($mol \cdot kg^{-1} \cdot s^{-1} \cdot bar^{-1/2}$)
- $k_2$ reaction rate constant for the 2nd rate equation ($mol \cdot kg^{-1} \cdot s^{-1} \cdot bar^{-1/2}$)
- $k_3$ reaction rate constant for the 3rd rate equation ($mol \cdot kg^{-1} \cdot s^{-1} \cdot bar^{-1/2}$)
- $k_{gl}$ mass transfer coefficient for component $i$ ($m \cdot s^{-1}$)
- $L$ length of reactor ($m$)
- $M_i$ molecular weight of component $i$ ($g \cdot mol^{-1}$)
- $N$ number of components
- $N_i$ molar flux ($mol \cdot m^{-2}$)
- $P$ total pressure (bar)
- $P_i$ partial pressure (bar)
- $P_{atm}$ atmospheric pressure (bar)
- $P_{sh}$ shell pressure (bar)
- $P_{ps}$ permeability of hydrogen through Pd–Ag layer ($mol \cdot m^{-1} \cdot s^{-1} \cdot Pa^{-1/2}$)
- $P_0$ pre-exponential factor of hydrogen permeability ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$)
- $R$ universal gas constant ($J \cdot mol^{-1} \cdot K^{-1}$)
- $Re$ Reynolds number
- $R_i$ inner radius of Pd–Ag layer ($m$)
- $R_o$ outer radius of Pd–Ag layer ($m$)
- $r_i$ reaction rate of component $i$ ($mol \cdot kg^{-1} \cdot s^{-1}$)
- $r_{1s}$ rate of reaction for hydrogenation of CO ($mol \cdot kg^{-1} \cdot s^{-1}$)
- $r_{2s}$ rate of reaction for hydrogenation of CO$_2$ ($mol \cdot kg^{-1} \cdot s^{-1}$)
- $r_{3s}$ reversed water–gas shift reaction ($mol \cdot kg^{-1} \cdot s^{-1}$)
- $S_{ch}$ Schmidt number of component $i$ ($-$)
- $T$ bulk gas phase temperature ($K$)
- $T_{ref}$ reference temperature used in the deactivation model ($K$)
- $T_s$ temperature of solid phase ($K$)
- $T_{sat}$ saturated temperature of boiling water at operating pressure (K)
- $T^h$ temperature of coolant stream, in first reactor ($K$)
- $T^{tu}$ temperature of coolant stream, in second reactor ($K$)
- $t$ Time ($s$)
- $U^{sh}$ overall heat transfer coefficient between coolant and process streams ($W \cdot m^{-2} \cdot K^{-1}$)
- $U$ superficial velocity of fluid phase ($m \cdot s^{-1}$)
- $u_f$ linear velocity of fluid phase ($m \cdot s^{-1}$)
- $y^{sh}_{i}$ mole fraction of component $i$ in the fluid phase in shell ($mol^{-1}$)
- $y^{sh}_{i,s}$ mole fraction of component $i$ in the solid phase in shell
- $y^{tu}_{i,s}$ mole fraction of component $i$ in the fluid phase in tube side ($mol^{-1}$)
- $y^{tu}_{i}$ mole fraction of component $i$ in the solid phase in tube side ($mol^{-1}$)
- $z$ axial reactor coordinate ($m$)
- $\alpha$ tortuosity of catalyst ($-$)
- $\Delta$ thickness of membrane ($m$)
- $\varepsilon_{vb}$ void fraction of catalytic bed ($-$)
- $\varepsilon_{v}$ void fraction of catalyst ($-$)
- $\mu$ viscosity of fluid phase ($kg \cdot m^{-1} \cdot s^{-1}$)
- $\rho$ density of fluid phase ($kg \cdot m^{-3}$)
- $\rho_{vb}$ density of catalytic bed ($kg \cdot m^{-3}$)
- $\rho_{v}$ density of catalyst ($kg \cdot m^{-3}$)
- $\eta$ catalyst effectiveness factor ($-$)
- $\tau$ tortuosity of catalyst ($-$)
- $\Omega$ auxiliary variable ($-$)

**Greek letters**

- $\alpha$ activity of catalyst
- $\beta$ mass transfer coefficient for component $i$ ($mol \cdot s^{-1} \cdot Pa^{-1/2}$)
- $\gamma$ void fraction of catalytic bed ($-$)
- $\rho$ density of fluid phase ($kg \cdot m^{-3}$)
- $\Omega$ auxiliary variable ($-$)
- $\Delta$ thickness of membrane ($m$)
- $\varepsilon$ void fraction of catalyst ($-$)
- $\mu$ viscosity of fluid phase ($kg \cdot m^{-1} \cdot s^{-1}$)
- $\rho$ density of fluid phase ($kg \cdot m^{-3}$)
- $\rho_{vb}$ density of catalytic bed ($kg \cdot m^{-3}$)
- $\rho_{v}$ density of catalyst ($kg \cdot m^{-3}$)
- $\eta$ catalyst effectiveness factor ($-$)
- $\tau$ tortuosity of catalyst ($-$)
- $\Omega$ auxiliary variable ($-$)
- $\Delta$ thickness of membrane ($m$)

**Superscripts and subscripts**

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

**Equations**

equilibrium-based and an increase in temperature decreases the equilibrium conversion of CO. Therefore, achieving the highest temperature at the entrance with a gradual decrease toward the exit of the reactor in order to reach the highest removal rate of CO is a major issue in methanol synthesis.
is a high temperature water-cooled reactor that is combined in series with a low temperature gas-cooled reactor where partial conversion of CO to methanol is achieved. Reacting gas in the second reactor has low H\textsubscript{2} content resulting in a decreased performance in comparison with the first reactor. One way to enhance the performance of the gas-cooled reactor is to add hydrogen to the reacting gas selectively by using a membrane, shifting the chemical equilibrium towards the product side [12].

A membrane two-stage methanol synthesis reactor has been developed by Rahimpour and Lotfinejad [13]. This modified reactor combines the chemical and membrane conversion in one system and has these advantages: (1) Enhancement of CO conversion, overcoming the potential limitations imposed by thermodynamic equilibrium [12]; (2) Higher CO conversion relative to CO\textsubscript{2} conversion; (3) Improvement of kinetics-limited reactions in the first reactor as a result of higher feed temperature; (4) Enhancement of equilibrium-limited reactions due to a lower temperature in the second reactor; (5) Control of the stoichiometric number of reacting gases along the gas-cooled reactor by hydrogen diffusion through the membrane. In chemical processes, membrane conversion technologies are mainly used in reaction systems containing hydrogen and oxygen where inorganic membranes are dominantly implemented [14]. It has been observed that diffusion of hydrogen through palladium membranes can enhance the selectivity of hydrogenation [15]. The use of Pd membranes is hindered because palladium shows a transition from the \(\alpha\)-phase (hydrogen poor) to the \(\beta\)-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 \(\alpha\)-phase is 3% smaller than that of the \(\beta\)-phase, this transition leads to lattice strain, and consequently after a few cycles, to a deformity of the metal lattice [16]. In many hydrogen-related reaction systems, Pd-alloy membranes on a stainless steel support have been used as the hydrogen-permeable membrane [17]. A maximum value of hydrogen permeability is reached for an alloy with a silver content of 23 wt.% [18]. Despite numerous membranes developed and investigated, Pd and its alloy membranes are still the most widely employed membranes for transporting hydrogen because of their high permeability and selectivity, good surface properties and ability to catalyze the surface dissociation and reassociation of H\textsubscript{2} [19,20]. These membranes combine hydrogen transition with distinguishing properties such as resistance to high temperatures, solvents, and corrosion. The main reason for the development of Pd-based membranes is low costs as well as perm-selectivity combined with good mechanical, thermal and long-term stability [21]. Thick-walled palladium alloy membranes have shown good thermal stability against high temperature and the reactant atmospheres, in some studies with thin palladium or palladium alloy films deposited by electroless plating stability problems have been encountered at temperatures above 400–500 °C. These properties make palladium-based membranes, such as Pd–Ag membranes, interesting alternatives for use in the petrochemical industry.

Membrane two-stage methanol synthesis reactors are similar to their conventional counterparts with the exception that in this system, the walls of tubes in the gas-cooled reactor are coated with a Pd–Ag membrane. Generally, feed synthesis gas can be introduced into the gas-cooled reactor with two different flow configurations in relation to the reacting gas flow – co-current (in parallel flow) and counter-current (in counter-flow) [22–24].

In previous works, the authors have studied co-current and counter-current modes of operation for an industrial and fluidized-bed membrane two-stage methanol synthesis reactor [25,26]. These studies revealed that implementing a counter-current flow configuration yields higher methanol production than when a co-current configuration is used.

The objective of the present study is to compare the performance of membrane two-stage methanol synthesis reactors in co-current and counter-current configurations in terms of CO removal rates, catalyst activity and hydrogen permeation rates. This comparison shows that the counter-current mode yields a higher conversion of CO with a higher CO removal rate and higher hydrogen permeation rate compared with the co-current mode. However, in the co-current mode, the catalyst activity is maintained at higher levels resulting in longer catalyst life.

2. Reactor configurations

2.1. Conventional two-stage methanol synthesis reactor

The catalyst is packed in vertical tubes of the gas-cooled reactor and the shell side of water-the cooled reactor. Reactions of methanol synthesis are performed over commercial CuO/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts. 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 the same reactor. Outlet synthesis gas then enters the tubes of the first reactor and the chemical reaction is initiated by the 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 the reacting gas mixture is left directing to the catalyst shell side of the second reactor and its temperature is continuously reduced through the catalyst bed. Finally, the product is removed from the side stream of the second reactor.

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

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

2.2. Membrane two-stage methanol synthesis reactor in co-current and counter-current modes

Methanol synthesis in membrane two-stage reactors is similar to their conventional two-stage counterparts, with the exception that in the membrane 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) in the membrane two-stage reactor permits hydrogen diffusion through the Pd–Ag membrane layer. On the other hand, in this system, mass and heat transfer occur simultaneously be-
between the shell and the tubes, while in the conventional-type only a heat transfer occurs between them.

The difference between methanol synthesis in counter-current and co-current modes is in the direction of synthesis gas flowing through the tubes of the second reactor. In counter-current configuration, feed synthesis gas is fed to the tubes in opposite direction to the reacting gas from the top of the reactor, whereas in co-current configuration, synthesis gas flows through the tubes in the same direction as the reacting gas mixture stream in the shell side. Fig. 1 is a schematic diagram of a membrane two-stage methanol synthesis reactor in counter-current and co-current modes for CO conversion to methanol.

In this simulation study, the Pd–Ag layer thickness is 0.8 mm and all specifications for the membrane two-stage system in the first and second reactors are the same as conventional reactors as summarized in Tables 1 and 2.

### 3. Mathematical model

The mathematical model for the simulation of the membrane two-stage methanol synthesis reactor was developed based on the following assumptions: (1) All streams are considered as 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; Fig. 2 is the schematic diagram of anelemental volume of a membrane reactor in co-current and counter-current modes.

#### 3.1. Water-cooled reactor (first stage)

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

<table>
<thead>
<tr>
<th>Feed composition (mol%):</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>8.68</td>
</tr>
<tr>
<td>CO₂</td>
<td>8.49</td>
</tr>
<tr>
<td>H₂</td>
<td>64.61</td>
</tr>
<tr>
<td>CH₄</td>
<td>9.47</td>
</tr>
<tr>
<td>N₂</td>
<td>8.2</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.1</td>
</tr>
<tr>
<td>CH₃OH</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)</td>
<td>7.1</td>
</tr>
<tr>
<td>Pressure [bar]</td>
<td>76</td>
</tr>
</tbody>
</table>
\[ \varepsilon_i \partial y_{iu}^{\text{th}} / \partial t = k_i (y_i^\text{th} - y_i^\text{in}) + \eta_r \rho_p a \quad i = 1, 2, \ldots, N - 1 \]  

(1)

\[ \rho_c C_p \partial T_{iu}^{\text{th}} / \partial t = a_i h_i (T_i^\text{th} - T_i^\text{in}) + \rho_c \sum_{j=1}^{N} \eta_f (\Delta H_f j) \]  

(2)

where \( y_i^\text{in} \) and \( T_i^\text{in} \) are the mole fraction and temperature of the solid phase in the 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:

\[ \varepsilon_i C_i \partial y_{iu}^{\text{th}} / \partial t = -F_{iu} \partial y_{iu}^{\text{th}} / \partial z + a_i c_i k_i (y_i^{\text{th}} - y_i^\text{in}) \quad i = 1, 2, \ldots, N - 1 \]  

(3)

\[ \varepsilon_i C_i C_{ps} \partial T_{iu}^{\text{th}} / \partial t = -F_{iu} \partial T_{iu}^{\text{th}} / \partial z + a_i h_i (T_i^{\text{th}} - T_i^\text{in}) + \pi D_i U_i (T_i^{\text{th}} - T_i^\text{in}) \]  

(4)

where \( y_i^{\text{th}} \) and \( T_i^{\text{th}} \) are the fluid-phase mole fraction and temperature in the tube side; also \( F_{iu} \) and \( A_i \) are total molar flow rate and cross-section in each tube, respectively. The boundary conditions are unknown and further details are discussed in the section concerning the numerical solution.

\[ \begin{align*}
    z = 0; \quad F_i^{\text{in}} = F_i, \\
    y_i^{\text{in}} = y_{iu}, \quad T_i^{\text{in}} = T_i
\end{align*} \]  

(5)

The initial conditions are:

\[ \begin{align*}
    t = 0; \quad y_i^{\text{in}} = y_{iu}, \quad y_i^{\text{in}} = y_{iu}, \quad T_i^{\text{in}} = T_i, \quad T_i^{\text{in}} = T_i, \quad a = 1
\end{align*} \]  

(6)

### 3.2.1. Shell side

**Overall mass balance:**

\[ \begin{align*}
    \varepsilon_i \partial y_{iu}^{\text{sh}} / \partial t = -F_{iu} \partial y_{iu}^{\text{sh}} / \partial z + a_i c_i k_i (y_i^{\text{sh}} - y_i^\text{in}) + \eta_f \rho_p a_i \quad i = 1, 2, \ldots, N - 1
\end{align*} \]  

(7)

where \( c_i \) and \( F_{iu} \) are total concentration and flow rate in the tube side. Mass and energy balance equations for the fluid phase are given as:

\[ \begin{align*}
    \varepsilon_i \partial y_{iu}^{\text{sh}} / \partial t = & -F_{iu} \partial y_{iu}^{\text{sh}} / \partial z + \eta_f \rho_p a_i \left( \sqrt{P_{iu}^{\text{sh}}} - \sqrt{P_{iu}^\text{in}} \right) \\
    \rho_c C_p \partial T_{iu}^{\text{sh}} / \partial t = & a_i h_i (T_i^{\text{sh}} - T_i^\text{in}) + \rho_c \sum_{j=1}^{N} \eta_f (\Delta H_f j)
\end{align*} \]  

(8)

The boundary conditions are as follows:

\[ \begin{align*}
    z = L; \quad y_i^{\text{out}} = y_{iu}, \quad T_i^{\text{out}} = T_i
\end{align*} \]  

(9)

when \( \eta_f = 0 \), the membrane is not permeable to hydrogen and the model is used for conventional two-stage systems.

### 3.3. Equilibrium model

Equilibrium conversions can be calculated by solving two reaction equilibrium expressions simultaneously. Equilibrium constants for reactions (A1) and (A2), which are presented in Appendix A, are as follows:

\[ K_{p1} = \frac{F_{\text{CH}_3\text{OH}} (F)^2}{F_{\text{CO}} (H_2)} \]  

(10)

\[ K_{p2} = \frac{F_{\text{CO}} (H_2)}{F_{\text{CO}} (F)} \]  

(11)

Reaction (A3) is not necessary for thermodynamic analysis because it is a linear combination of the first two reactions – (A1) and (A2) [27]. The equilibrium constants of reactions (A1) and (A3), \( K_{p1} \) and \( K_{p3} \), have been identified as functions of temperature and pressure by Klier et al. [28]:

\[ K_{p1} = \frac{3.27 \times 10^{-13} \exp(11.678/T)}{1 - (1.95 \times 10^4 \exp(1703/T))^2} \]  

(12)

\[ K_{p3} = \frac{3.823 \times 10^{-13} \exp(11.678/T)}{1 - (1.95 \times 10^4 \exp(1703/T))^2(1 - 4.24 \times 10^{-4} \exp(1107/T))^2} \]  

(13)

\[ K_{p2} = K_{p3} / K_{p1} \]  

(14)

These equations can be applied to estimate equilibrium conversion by defining \( X_e \) and \( Y_e \) as the moles of \( \text{CH}_3\text{OH} \) and \( \text{H}_2\text{O} \) formed, respectively. These are used for membrane methanol reactors and when there is no membrane, the term \( T_{i}^{\text{in}} - T_{i}^{\text{out}} \), which represents additional hydrogen in reacting gas, is zero. Material balances around the methanol reactor are:

\[ F_{\text{CH}_3\text{OH},\text{in}} = F_{\text{CH}_3\text{OH},\text{in}} + X_e \]  

(15)

\[ F_{\text{H}_2\text{O},\text{in}} = F_{\text{H}_2\text{O},\text{in}} + Y_e \]  

(16)

\[ F_{\text{CO}_2} = F_{\text{CO}_2,\text{in}} - Y_e \]  

(17)

\[ F_{\text{CO}} = F_{\text{CO},\text{in}} - X_e + Y_e \]  

(18)

\[ F_{H_2} = F_{H_2, \text{in}} - 2X_e - Y_e + F_{H_2, \text{in}} - F_{H_2, \text{out}} \]  

(19)

\[ F_N = F_{N,\text{in}} \]  

(20)

Summation of Eqs. (19)-(24) results in the total flow rate of reaction side gas:
\[ F_T = F_m - 2X_F + F_{p_{\text{H}_2})} - F_{p_{\text{H}_2} \text{ex}} \]  
(27)

Substitution of Eqs. (16)–(25) into Eqs. (14) and (15) yields two equations with two unknown extents of reaction, \( X_F \) and \( X_F \). These equations can be solved numerically, but it has been discovered advantageous to work with the logarithms of both. The resulting equations used in the calculations are:

\[ F_1(X, Y) = \ln(K_{p1}) - \ln \left( \frac{F_{\text{CH}_{3}OH}}{F_{\text{H}_2}} \right)^{\frac{1}{2}} \]  
(28)

\[ F_2(X, Y) = \ln(K_{p2}) - \ln \left( \frac{F_{\text{CO}}F_{\text{H}_2}}{F_{\text{CO}_2}F_{\text{H}_2}} \right) \]  
(29)

Generally, convergent multi-dimensional Newton’s method in Fortran PowerStation 4.0 numerical recipes was used to solve the model equilibrium Eqs. (28) and (29).

3.4. Deactivation model

The deactivation model of the CuO/ZnO/Al2O3 catalyst has been studied by several researchers; however, the model suggested by Hanken was found to be suitable for industrial applications [29]:

\[ \exp \left( -\frac{E_d}{\bar{R}} \right) \left( \frac{1}{T_i} - \frac{1}{T_o} \right) a^2 \frac{da}{dt} = -K_d \]  
(30)

where \( E_d, T_i \), and \( K_d \) are activation energy, reference temperature and catalyst deactivation constant, respectively. The numerical value of \( E_d = 91,270 \text{ J/mol} \), \( T_o = 513 \text{ K} \), and \( K_d = 0.00439 \text{ h}^{-1} \) [29]. The above model has been fitted with industrial operating conditions and is the only case for simulation and modeling of industrial plants.

3.5. Hydrogen permeation in the Pd/Ag membrane

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

\[ j_i = \frac{Z_i}{\bar{R}} \left( \sqrt{P_i^{\text{in}} - \sqrt{P_i^{\text{in}}} \right) \]  
(31)

where \( P_i \) is the pressure of hydrogen on the two sides of the membrane. The permeation rate constant \( Z_i \) and the pre-exponential factor \( P_0 \) above 200 °C are reported as \( 6.33 \times 10^{-8} \text{ (mol/m}^2 \text{s Pa)}^{\frac{1}{2}} \) and activation energy \( E_p = 15.7 \text{kJ/kmol} \) [31,32].

4. Numerical solution

The fundamental structure of the model includes partial differential equations of mass and energy conservation in solid and fluid phases, 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 solution stage. In order to solve the set of reactor model equations, a steady-state simulation has been used prior to a dynamic simulation that exports initial values to the dynamic simulator.

4.1. Steady-state simulation

Steady-state model solution of the two-stage methanol reactor is performed by equaling all the time-variation of the states to zero and also considering a fresh catalytic bulk with the activity of unity. In this way, the initial conditions for temperature and concentration are determined for the dynamic simulation.

After rewriting the model equations, a set of differential algebraic equations (DAEs) is obtained for both co-current and counter-current modes. This set of equations is changed to non-linear algebraic equations (NAEs) using backward finite difference approximation. The NAEs are boundary value problem which has been solved using the shooting method in counter-current mode and trial and error method in co-current mode.

4.1.1. Solution procedure for co-current mode

In co-current mode, the calculation was started with initial guesses for \( T_i \) and \( y_{\text{in}} \), which are unknown (initial conditions). The initial conditions were calculated using the Gauss–Newton method replaced by its previous value in subsequent calculations. Substitution was continued until the convergence criterion was met.

4.1.2. Solution procedure for counter-current mode

In counter-current mode, the inlet feed synthesis gas temperature \( T_o \) and hydrogen mole fraction \( y_{\text{in}} \) to the water-cooled reactor are unknown (initial conditions), whereas the temperature \( T_i \) and hydrogen mole fraction \( y_i \) of the feed synthesis gas stream to the gas-cooled are known (final condition). The shooting method converts the boundary-value problem to an initial-value problem. Solution is possible by guessing values for \( T_i \) and \( y_{\text{in}} \) for the heated feed synthesis gas to the first stage. The first and second stages were divided into 14 and 16 nodes, respectively, and then the Gauss–Newton method was used to solve the nonlinear algebraic equations in each node. In the end, the calculated values of temperature \( T_i \) and hydrogen mole fraction \( y_i \) of the fresh feed synthesis gas were compared with the actual values. This procedure was repeated until the specified terminal values were obtained within a small convergence criterion.

4.2. Solution of the dynamic model

The results of steady-state simulations are used as initial conditions for time integration of dynamic state equations in each node through the two-stage methanol synthesis reactor. The set of dynamic equations of the deactivation model and conservation laws consist of simultaneous ordinary and partial differential equations, as well as algebraic equations due to auxiliary correlations, kinetics and thermodynamics of the reaction system. The set of equations

Table 3

Comparison between model results with plant data for fresh catalyst.

<table>
<thead>
<tr>
<th>Product condition</th>
<th>Plant</th>
<th>Predicted</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (molt):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃OH</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>-3.43</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0709</td>
<td>0.0764</td>
<td>-7.16</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.0234</td>
<td>0.0211</td>
<td>-3.55</td>
</tr>
<tr>
<td>H₂</td>
<td>0.5519</td>
<td>0.5323</td>
<td>-3.55</td>
</tr>
<tr>
<td>N₂/Ar</td>
<td>0.0968</td>
<td>0.0906</td>
<td>-6.5</td>
</tr>
<tr>
<td>CH₄</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>

have been separated with respect to the axial coordinate. Modified Rosenbrock formula of order 2 has been applied to discrete equations in each node along the reactor to integrate the set of equations with respect to time. The process duration has been considered to be 1400 operating days.

5. Results and discussion

5.1. Model validation

The validation of steady-state and dynamic models for co-current and counter-current configurations along the conventional two-stage methanol synthesis reactor with plant data has previously been performed by Rahimpour et al. and good agreement between the daily plant data and the simulation data was observed [25].

5.1.1. 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 (\( z_{th} = 0 \)) under design specifications. Input data is presented in Tables 1 and 2, respectively. The model results and data of the plant are tabulated in Table 3. It was observed that the steady-state model functioned acceptably under industrial conditions and the results of simulations were in good agreement with daily-real plant data.

5.2. Dynamic model validation

Validation of the dynamic model was performed by comparing simulation results with process history data of a single-type meth-

### Table 4

Comparison between predicted methanol production rate and plant data.

<table>
<thead>
<tr>
<th>Time (day)</th>
<th>Plant (ton/day)</th>
<th>Predicted (ton/day)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>295.0</td>
<td>308.80</td>
<td>2.93</td>
</tr>
<tr>
<td>100</td>
<td>296.5</td>
<td>297.03</td>
<td>0.18</td>
</tr>
<tr>
<td>200</td>
<td>302.6</td>
<td>289.10</td>
<td>−4.46</td>
</tr>
<tr>
<td>300</td>
<td>284.3</td>
<td>283.09</td>
<td>−0.44</td>
</tr>
<tr>
<td>400</td>
<td>277.9</td>
<td>278.19</td>
<td>0.10</td>
</tr>
<tr>
<td>500</td>
<td>278.2</td>
<td>274.03</td>
<td>−1.50</td>
</tr>
<tr>
<td>600</td>
<td>253.0</td>
<td>270.41</td>
<td>6.88</td>
</tr>
<tr>
<td>700</td>
<td>274.0</td>
<td>267.19</td>
<td>−2.48</td>
</tr>
<tr>
<td>800</td>
<td>268.1</td>
<td>264.30</td>
<td>−1.65</td>
</tr>
<tr>
<td>900</td>
<td>275.5</td>
<td>261.67</td>
<td>−5.02</td>
</tr>
<tr>
<td>1000</td>
<td>274.6</td>
<td>255.25</td>
<td>−5.58</td>
</tr>
<tr>
<td>600</td>
<td>262.9</td>
<td>257.02</td>
<td>−2.24</td>
</tr>
<tr>
<td>1200</td>
<td>255.2</td>
<td>255.18</td>
<td>−0.05</td>
</tr>
</tbody>
</table>

Fig. 3. Profiles of (a) temperature and (b) catalyst activity versus time and length for a membrane two-stage methanol synthesis reactor in co-current mode.

Fig. 4. Profiles of (a) CO removal rate and (b) CO mole fraction versus time and length.
anol synthesis reactor. The predicted results for the production rate and the corresponding observed data of the plant are listed in Table 4. It was demonstrated that the model carried out satisfactorily under industrial conditions and a good agreement was observed between the simulation data and daily plant data.

A parametric analysis was performed to address the vital issues, such as CO mole fraction, CO removal rate, temperature and catalyst activity profiles along the reactor. Fig. 3a and b illustrates the reactor temperature and catalyst activity profiles versus time and length in co-the current mode for a membrane two-stage methanol

Fig. 5. Profiles of the temperature and activity along co-current and counter-current reactor configurations for (a) 1st and (b) 1400th days.

Fig. 6. Profiles of the CO mole fraction and removal rate along co-current and counter-current reactor configurations for (a) 1st, (b) 100th, (c) 600th, and (d) 1400th days.
synthesis reactor. In the first stage, temperature of the reacting gas mixture in first days is higher than in the second stage due to higher conversion and freshness of catalyst. Moreover, temperature of the reacting gas mixture in both stages decreases with time because the heat of reaction is continuously removed by the water and gas coolants. However, the capability of the coolant gas to remove reaction heat is less than coolant water, as shown in Fig. 3a. Minimum activity is observed near the first reactor inlet, which is exposed to higher temperatures at different times. In the gas-cooled reactor, catalyst must have a lower temperature, which improves catalyst activity and the equilibrium constant, as shown in Fig. 3b. Also, this figure shows that during the operating time, the catalyst is deactivated as a result of poisoning and thermal sintering – the loss of catalyst active surface area owing to crystallite growth of either the support material or the active phase.

Fig. 4a and b is a three-dimensional plot of CO mole fraction and CO removal rate along the reactor length and time in co-current configuration for a two-stage membrane methanol synthesis reactor. CO mole fraction decreases along the reactor and increases with time because of catalyst deactivation, as shown in Fig. 4a. On the other hand, CO removal rate increases along the reactor and decreases as time passes (see Fig. 4b).

5.3. Comparison of co-current and counter-current modes

Fig. 5a and b shows the comparison between the temperature and catalyst activity profiles along co-current and counter-current reactor configurations for the 1st and the 1400th days. As can be seen in this figure, the first reactor operates at a lower temperature in the co-current mode compared with the counter-current configuration because feed synthesis gas in this stage is preheated more efficiently in the counter-current mode along the second stage. The gas-cooled reactor operates at a higher temperature in the counter-current mode than in the co-current mode, while an inverse behavior is observed near the reactor outlet. Also, the higher temperature of hydrogen is observed from 8 m to 13.2 m of the second reactor for the co-current configuration, while for lengths above 13.2 m, counter-current mode has a higher hydrogen permeation rate. Consequently, counter-current configuration is more suitable from the viewpoint of carbon monoxide removal.

6. Conclusion

Carbon monoxide is the most abundant and widely distributed air pollutant. The catalytic hydrogenation of carbon monoxide to methanol represents an effective method for preventing this side effect. In this paper, a Pd–Ag membrane was used in the second reactor of a two-stage methanol synthesis process and the effect of flow type on the performance of this system was investigated in terms of CO removal rate, catalyst activity and hydrogen permeation rate. The results show that in co-current configuration, activity of catalyst is maintained at a higher level compared with favorable catalyst temperature profile, which results in longer catalyst life. CO removal and hydrogen permeation rate, however, are lower in this configuration due to lower heat transfer. It should be noted that hydrogen permeation has a positive effect on the rate of CO removal. Therefore, optimization of key parameters such as CO mole fraction, temperature and catalyst activity can determine which configuration of flow is more suitable for the reactor.

Appendix A. 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:

\[ \text{CO} + 2\text{H}_2 \leftrightarrow \text{CH}_3\text{OH} \quad \Delta H_{298} = -90.55 \text{ kJ/mol} \]  \hspace{1cm} (A1)

\[ \text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298} = +41.12 \text{ kJ/mol} \]  \hspace{1cm} (A2)
Table A.1
Reaction rate constants [33].

<table>
<thead>
<tr>
<th>K – A exp (B/RT)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₁</td>
<td>4.89 ± 0.29 x 10⁷</td>
<td>-113,000 ± 300</td>
</tr>
<tr>
<td>K₂</td>
<td>9.64 ± 7.30 x 10⁷</td>
<td>-152,900 ± 11,800</td>
</tr>
<tr>
<td>K₃</td>
<td>1.09 ± 0.07 x 10⁷</td>
<td>-87,500 ± 300</td>
</tr>
</tbody>
</table>

Table A.2
Adsorption equilibrium constants [33].

<table>
<thead>
<tr>
<th>K – A exp (B/RT)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kₒ</td>
<td>2.16 ± 0.44 x 10⁻⁵</td>
<td>46,800 ± 800</td>
</tr>
<tr>
<td>Kₑ</td>
<td>7.05 ± 1.39 x 10⁻⁷</td>
<td>61,700 ± 800</td>
</tr>
<tr>
<td>(Kₒ)(Kₑ)(Kₚ)</td>
<td>6.37 ± 2.88 x 10⁻⁹</td>
<td>84,000 ± 1400</td>
</tr>
</tbody>
</table>

Table A.3
Reaction equilibrium constants [33].

<table>
<thead>
<tr>
<th>K – A exp (B/RT)</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₁₁</td>
<td>5139</td>
<td>12,621</td>
</tr>
<tr>
<td>K₁₂</td>
<td>-2073</td>
<td>-2,029</td>
</tr>
<tr>
<td>K₁₃</td>
<td>3066</td>
<td>10,592</td>
</tr>
</tbody>
</table>

CO₂ + 3H₂ → CH₃OH + H₂O  ΔH₂₉₈ = -49.43 kJ/mol (A3)

Reactions (A1)–(A3) 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. [33]. The rate equations combined with the equilibrium rate constants [34] provide enough information about kinetics of methanol synthesis. The correspondent rate expressions due to the hydrogenation of CO, CO₂ and the reversed water–gas shift reactions are:

\[
\begin{align*}
R₁ &= \frac{k₁Kₒ\left[COf_{Hi}^{1/2} - f_{CH₂O}/(f_{H₂}^{1/2}Kₚ)\right]}{(1 + KₚCOf_{CO} + KₚCO₂f_{CO₂})} f_{H₂}^{1/2} + (KₒH₂O/KₚH₂O)f_{H₂O} \\
R₂ &= \frac{k₂Kₒ\left[COf_{H₂} - f_{H₂O}f_{CO}/Kₚ\right]}{(1 + KₚCOf_{CO} + KₚCO₂f_{CO₂})} f_{H₂}^{1/2} + (KₒH₂O/KₚH₂O)f_{H₂O} \\
R₃ &= \frac{k₃Kₒ\left[COf_{H₂}^{1/2} - f_{H₂O}f_{Hi}/(f_{H₂}^{1/2}Kₚ)\right]}{(1 + KₚCOf_{CO} + KₚCO₂f_{CO₂})} f_{H₂}^{1/2} + (KₒH₂O/KₚH₂O)f_{H₂O}
\end{align*}
\]

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.

Appendix B. Auxiliary correlations

B.1. Mass transfer correlations

In the current work, mass transfer coefficients for the components have been taken from Cussler [35]. These are mass transfer coefficients between gas phase and solid phase.

\[
k_{gi} = 1.17Re^{−0.42}Sc_{i}^{−0.67}u_p x 10^{3}
\]  

(B1)

where the Reynolds and Schmidt numbers have been defined as:

\[
Re = \frac{2K_p u_p}{\mu} \\
Sc_i = \frac{\mu}{\rho D_m} \times 10^4
\]

And the diffusivity of component i in the gas mixture is given by [36].

\[
D_m = \frac{1 - y_i}{\sum_{j} \frac{y_i}{D_{mj}^{1/2}}}
\]

(B4)

And also the binary diffusivities are calculated using the Fuller–Schetter–Giddins equation that is reported by Reid and his co-workers [37]. In the following Fuller–Schetter–Giddins correlation, vᵢ, Mᵢ are the critical volume and molecular weight of component i which are reported in Table B.1 [38].

\[
D_{ij} = \frac{10^{-7}T^{3/2} \frac{1}{R_i} + \frac{1}{R_j}}{P_i^{1/2} + P_j^{1/2}}
\]

(B5)

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 (τ).

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:

\[
\frac{1}{U_{shell}} = \frac{1}{h_i} + \frac{A_i}{2\pi T K_{m}} + \frac{A_i}{h_i h_0}
\]

(B6)

where \(h_i\) is the heat transfer coefficient between the gas phase and reactor wall and is obtained by the following correlation [39]:

\[
\frac{h_i}{c_p \mu H} \left( \frac{C_p H}{K} \right)^{2/3} = \frac{0.458 \left( \frac{\rho u_d p_H}{\mu} \right)^{-0.407}}{\varepsilon_W}
\]

(B7)

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, \(\rho, \mu\) are density and viscosity of gas, respectively and \(\varepsilon_W\) is void fraction of catalyst bed. In equation (B6), \(h_i\) is the heat transfer coefficient of boiling water in the shell side which is estimated by the following equation [40]:

\[
h_w = 7.96(T - T_{sat})^{3/4} \left( \frac{P}{P_a} \right)^{0.4}
\]

(B8)

And \(T\) 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 \(P_a\) 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 trans-
fer coefficient between bulk gas phase and solid phase \( (h_s) \), Eq. (B7) is applicable.

References