Process Safety Aspects in Water-Gas-Shift (WGS) Catalytic Membrane Reactors Used for Pure Hydrogen Production

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Abstract

The syngas produced by coal gasification processes can be utilized in Pd-based water gas shift membrane reactors for the production of pure H\textsubscript{2}. Pd/Alloy composite membrane reactors exhibit comparative advantages over traditional packed bed reactors such as simultaneous reaction/separation in one compact unit and increased reaction yields. Furthermore, the development of comprehensive process intensification strategies could further enhance membrane reactor performance resulting in a substantially smaller and functional, inherently safer, environmentally friendlier and more energy efficient process.

A systematic non-isothermal modeling framework under both steady state and dynamic/transient conditions for a catalytic high temperature water-gas shift reaction in a Pd-based membrane reactor has been developed to characterize the dynamic behavior of the process system at various operating conditions from a process safety standpoint. In particular, various reaction conditions as well as key process variables such as feed temperature and flow rate, catalyst loading, driving force for H\textsubscript{2} permeation are considered as they are critically related to various safety aspects in the operation of a Pd-based membrane reactor. Within the proposed framework, process parameters and operating conditions which may induce hazards and compromise process safety are identified, analyzed and characterized. Finally, the proposed approach is evaluated through detailed simulation studies in an illustrative case study involving a real Pd-based membrane reactor used for pure hydrogen production and separation that exhibits complex behavior over a wide operating regime.

Keywords: Membrane reactors; hydrogen production and separation; process intensification; process safety; hazard identification and characterization.

1. Introduction

Hydrogen as an energy carrier holds the promise of leading to a more diversified and efficient energy economy that is less dependent on oil, while allowing critical problems such as environmental pollution and green-house gas emission rates to be responsibly addressed. In addition, all stakeholders involved in the development and structuring of such a global energy system need to be mindful of a new host of safety challenges as suggested by Pasman and Rogers.\textsuperscript{1}
In the meantime, from a technical standpoint, the natural abundance of coal is envisioned and expected to be one of the primary sources of hydrogen production in a hydrogen economy paradigm. In particular, the coal-based syngas produced at an Integrated Gasification Combined Cycle (IGCC) plant represents an attractive source for H\textsubscript{2} production combined with electricity generation and the synthesis of valuable chemicals. Within such a context, H\textsubscript{2} is being produced mainly through the water gas shift (WGS) reaction currently used in many significant industrial applications. The water gas shift reaction, a well known and intensively studied reaction, is exothermic with an equilibrium constant inversely proportional to temperature.

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^0_{298,K} = -41.2 \text{kJ mol}^{-1}
\]

Membrane reactors, in which WGS reaction and H\textsubscript{2} separation can take place simultaneously, enjoy significant comparative advantages over traditional packed bed reactor performance characteristics. Indeed, continuous removal of H\textsubscript{2} from the reaction zone shifts the equilibrium to the products side and as a result, significantly higher (compared to the thermodynamically limited one offered by traditional packed bed reactors) CO conversion level (≥95%) as well as very high H\textsubscript{2} recovery (≥90%) can be achieved.

In particular, Pd/Pd-Alloy composite membranes supported on porous metals (such as porous stainless steel, Inconel or Hastelloy), exhibit high permeability and H\textsubscript{2} selectivity, and their practical utilization at high temperature (300-500°C) and pressure (20-60 atm) has been demonstrated. Furthermore, the retentate stream with very low CO concentrations would be operationally appropriate for and compatible with the high pressure CO\textsubscript{2} sequestration step, while extra pure H\textsubscript{2} can be separated and recovered through a highly selective Pd-Based composite membrane. In particular, Pd/Pd-Alloy membranes supported on porous stainless steel or Inconel cylindrical tubes developed at the Center for Inorganic Membrane Studies, WPI are considered in the present research study. It should be pointed out that palladium membranes supported on porous substrates, like porous stainless steel, Inconel or Hastelloy, have several advantages such as a very thin Pd layer (3-20µm), good mechanical strength and very high H\textsubscript{2} flux. Furthermore, the porous metal supports can be integrated into the overall process system quite easily. Resistance to mechanical cracking and simplicity of the module construction are the additional benefits of porous metal supports. Finally, the specific fabrication method for Pd/Pd-Alloy composite membranes includes electroless plating which enables the manufacturer to scale up and readily apply the plating method to any geometry.

A considerable amount of research effort has been devoted to characterize the behavior and optimize the performance of WGS membrane reactors through the appropriate modeling framework informed by experimental results and empirical observations. Notably, the importance of thermal effects on membrane reactor operation and performance has been recognized by many researchers in the aforementioned body of pertinent literature. In particular, relatively large undesirable temperature gradients along the reactor could often be observed in the adiabatic mode of operation which is detrimental for membrane stability. Furthermore, non-isothermal reactor modeling methods can be used as a judicious guide for an economically favorable, safer and environmentally friendlier process design.

The primary research objective of the present study is to develop a comprehensive and practical model-based investigation and characterization of key process parameters and operating conditions that could potentially induce certain process hazards in Pd-based membrane reactor systems used for hydrogen production, and ultimately identify incidents where process safety could be compromised by following standard principles of Hazard and Operability (HAZOP) analysis.
in a spirit conceptually similar to the one in Chiappetta et al. Within the above context, issues related to root causes identification, scenario development, consequences characterization and precautionary action determination on the basis of adverse deviations in the total feed flow rate and temperature, \( \text{H}_2\text{O}:\text{CO} \) ratio, catalyst loading, reaction and permeate side pressures and purity of the feed from normal operating conditions are discussed with the aid of the proposed membrane reactor modeling framework and detailed simulation studies. Specifically, the paper is organized as follows: Section 2 contains a description of the main structural characteristics of the proposed Pd-based membrane reactor modeling framework, followed by Section 3 where the paper’s main results on membrane reactor safety issues during operation for hydrogen production are presented. Finally, a few concluding remarks are provided in Section 4.

2. Membrane Reactor Modeling Framework

A comprehensive, insightful and computationally tractable steady state and dynamic process modeling framework for a catalytic high temperature water-gas shift Pd-based membrane reactor used for hydrogen production and separation has been developed at non-isothermal conditions in order to identify and characterize potentially hazardous conditions and key factors that could compromise process safety. The proposed membrane reactor modeling framework has been developed under the following assumptions: the reactor shell is adiabatic, isobaric conditions on both reaction and permeate sides, ideal gas behavior is invoked, no poisoning of the membrane and/or the catalyst under the reaction conditions occurs, practically infinite selectivity of the membrane is offered and no significant mass or heat dispersion effects take place.

The Pd-based membrane reactor considered in this work has the shell and tube configuration as the one described in greater detail in the work of Ayturk et al. While the reaction is taking place in the shell side, extra pure \( \text{H}_2 \) can be obtained from the permeate side stream. The membrane reactor was composed of two concentric tubes in which the Pd-Based membrane was placed onto the outer surface of the stainless steel tube as depicted in Fig. 1. The mass and energy balance equations at steady and also unsteady state conditions were derived by using the principles of conservation of mass and energy. The geometry of the membrane reactor and the properties of the composite Pd membrane which were used in the model are listed in Table 1.

![Figure 1. Schematic diagram of a membrane reactor](image-url)
<table>
<thead>
<tr>
<th>Reactor dimensions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>I.D. of the shell casing [m]</td>
<td>2.54×10^{-2}</td>
</tr>
<tr>
<td>O.D. of the membrane tube [m]</td>
<td>1.27×10^{-2}</td>
</tr>
<tr>
<td>The total length of the membrane [m]</td>
<td>6.35×10^{-2}</td>
</tr>
<tr>
<td>Catalyst weight [g]</td>
<td>15</td>
</tr>
<tr>
<td>ε [-]</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Properties of the Pd/Inconel membrane\(^{11}\)**

- \(Q_o\) \(\text{[} \text{m}^3.\mu\text{m}/(\text{m}^2.\text{h.atm}^{0.5})\text{]}\) | 6322.7 |
- \(E_{\text{permeation}}\) \(\text{[kJ/mol]}\) | 15.6 |
- \(l\) (Pd Thickness) \(\text{[} \mu\text{m}\text{]}\) | 10     |

### 2.1 The steady state membrane reactor model

Under steady state conditions and the aforementioned assumptions, the following mass balance equations naturally arise:

(i) Mass balance equations for gas phase species in the reaction side:

\[
\frac{dF_{H_2}}{dz} = \rho_{Bulk} \cdot A_c \cdot L \cdot r_{H_2} - A_m \cdot J_{H_2} \tag{1}
\]

\[
\frac{dF_l}{dz} = \rho_{Bulk} \cdot A_c \cdot L \cdot r_l \tag{2}
\]

\[
J_{H_2} = \frac{Q}{l} \cdot \left( p_{H_2,\text{Reaction side}}^{0.5} - p_{H_2,\text{Permeate side}}^{0.5} \right) \text{ by Sievert’s Law} \tag{3}
\]

(ii) Mass balance equation for H\(_2\) in the permeate side:

\[
\frac{dF_{H_2}}{dz} = A_m \cdot J_{H_2} \tag{4}
\]

Furthermore, an energy balance equation in the reaction side takes the following form:

\[
\frac{dT_{Shell}}{dz} = \frac{(-r_l \rho_{Bulk} V_{Annulus})(-\Delta H_{Rxn}) - U A_m (T_{Shell} - T_{Tube})}{\sum F_i \cdot C_{pl_{Reaction side}}} \tag{5}
\]
Notice that the reaction side energy balance equation consists of the heat of reaction term, the term capturing the amount of heat being exchanged with the permeation side as well as the convective flux of energy term 5.

Finally, an energy balance equation in the permeate side can also be explicitly developed:

\[
\frac{dT_{\text{tube}}}{dz} = \frac{A_m \mu \left( H_{H_2}^{\text{shell}} - H_{H_2}^{\text{Permeate}} \right) + u A_m (T_{\text{shell}} - T_{\text{tube}})}{\sum F_i c_{pi}|_{\text{permeate side}}} \tag{6}
\]

Notice that both the amount of energy associated with the permeating H\textsubscript{2} and the heat exchange with the reaction side have been included into the above permeate side energy balance equation.

2.2 The unsteady state/dynamic membrane reactor model

For the spatially distributed process system under consideration, a standard transient energy balance equation which involves the heat produced by the reaction and the heat removed from the reaction side by means of H\textsubscript{2} permeation was added to the system of unsteady state (dynamic) mole balance equations for each species, resulting in a mathematical representation realized by a system of partial differential equations (infinite-dimensional). The membrane reactor length was then partitioned into N compartments (a spatial discretization technique known as lumped parameter approximation), and each one of them viewed and modeled as a standard continuous stirred-tank reactor (CSTR) (thus approximating the original infinite-dimensional problem by a finite-dimensional one). A system of ordinary differential equations (ODEs) representing unsteady state mass and energy balance equations for each CSTR in the above N compartments were then solved simultaneously using the MATLAB toolbox (ode23s) \textsuperscript{27}.

Within the above modeling framework, the mass balance equation for H\textsubscript{2} in the reaction side attains the following form:

\[
\frac{df_{H_2}|_{y+\Delta y}}{dt} = \frac{1}{C_{\text{Total}}^{\text{shell}} \Delta v_{\text{shell}}} \left[ f_{H_2}|_y F_{\text{Total}}^{\text{shell}}|_y - f_{H_2}|_{y+\Delta y} F_{\text{Total}}^{\text{shell}}|_{y+\Delta y} + r_{H_2}|_{y+\Delta y} \right] \Delta W - \frac{Q A_m}{l} \cdot \Delta P_{H_2}^{0.5} \tag{7}
\]

Notice that the mole balance equations for CO, CO\textsubscript{2} and H\textsubscript{2}O in the shell side and H\textsubscript{2} in the tube side can be written in a structurally similar manner as Equation 7. For a more detailed view of the model’s structure the interested reader is referred to the work with the name of “A Process Dynamic Modeling and Control Framework for Performance Characterization and Enhancement of Pd-Based Membrane Reactors” which will be published.

Furthermore, the energy balance equation in the reaction side can be expressed as follows:

\[
\frac{dT}{dt} = \frac{Q_{HF} - W_e - \sum F_i|_y (r_{H_2}|_{y+\Delta y} - r_{H_2}|_y) + (-\Delta H_{\text{Rx}}|_{y+\Delta y}) (r_{H_2}|_{y+\Delta y} \Delta W)}{\sum n_i|_{y+\Delta y} c_{pi}|_{y+\Delta y}} \tag{8}
\]

Notice that the shell side was assumed to be adiabatic with no shaft work occurring, and thus both \( Q \) and \( W_e \) equal to zero.

The appropriate set of boundary conditions and initial condition for a well-defined problem that also realistically captures operating conditions for the membrane reactor under consideration is as follows:

Boundary condition at the inlet: The molar flow rates of each gaseous species at the inlet stream of the catalytic zone are constant for all times.
Boundary condition at the exit: At the interface between the porous part and the catalytic area, species that enter the control volume exit it with no further change.

\[
\frac{\partial F_i}{\partial y} = 0
\]  

Initial conditions: During the start-up of the reactor, only steam and inert gas are flowing through the reactor before admitting the reactants into the reactor. Reaction and permeate side temperatures are considered to be equal to the feed temperature before the reaction starts.

The effective radial heat conductivity and the wall heat transfer coefficients were calculated by using the correlations reported by Dixon and Cresswell. The improved equation for the overall heat transfer coefficient proposed by Dixon was used in the model. Furthermore, the heat transfer resistance needed to calculate the overall heat transfer coefficient \((U)\), was predicted with the same method proposed by Madia et al. for methane steam reforming in a membrane reactor.

Finally, the empirical reaction rate equation suggested by Hla et al. was utilized in the model for the high temperature water gas shift kinetics, and the thermodynamic properties listed in the NIST Chemistry Web Book for all gas species involved were used for the equilibrium constant calculations.

3. Main Results and Discussion

3.1 The membrane reactor under steady state and non-isothermal conditions

The above modeling framework for the Pd-based membrane reactor served as the basis for the identification of key process variables as well as operating conditions capable of inducing potentially hazardous situations where process safety could be compromised and, standard principles of Hazard and Operability (HAZOP) analysis were followed and applied to identify and hopefully prevent potential process risks to personnel, environment, equipment integrity and/or the efficiency or economics of the process. In particular, the causes and consequences for each of the hypothesized scenarios involving deviations of one of the key process variables considered in the present study from the desirable operating conditions were determined in a systematic way within the context of HAZOP analysis. A guide word such as “MORE, LESS or NO” is normally assigned to one of the selected variables and deviations in all other process variables are identified and monitored. One of course should be mindful of the fact that an analysis involving the whole process plant is time-consuming and requires a large amount of work by a group of experts. Throughout the conduct of the safety analysis in our study, only the Pd-based WGS membrane reactor unit of the IGCC plant was evaluated using HAZOP analysis. In particular, a non-isothermal model-based membrane reactor performance assessment was performed by analyzing the particular effects on process operation and performance of the feed temperature, feed flow rate, bulk catalyst density, the H\(_2\)O:CO mole ratio, reaction side total pressure, membrane area and permeate side pressure on CO conversion, H\(_2\) recovery and reaction side temperature profile. Root causes, consequences and precautionary measures associated with any deviations in the operating conditions from the desirable ones were identified and evaluated in order to ensure process safety while maintaining the performance target levels at \(X_{\text{CO}} = 98\%\) CO conversion and \(R_{\text{H}_2} = 95\%\) hydrogen recovery. At the same time, the objective to keep the maximum temperature in the reaction side below the safety limit of membrane of 500°C was pursued.
3.1.1 Effect of feed temperature

The identification and characterization of the optimum feed temperature needs to be performed by considering both the efficiency of the process and integrity of the Pd-based membrane. On one hand, the feed temperature should be higher than the threshold temperature of the WGS catalyst and the reaction rate should be high enough to achieve the performance target levels. The rate of permeation is also dependent on temperature and high permeation rates are favored at high temperatures. On the other hand, if the feed temperature exceeds a certain limit, the resulting high reaction side temperature would cause a deterioration of the Pd-based membrane.

Notice that pure Pd-based membranes have a minimum and maximum working temperature. The reaction side temperature should be higher than 300°C to avoid the α-β phase transition of palladium hydride. Once the palladium hydride is formed, the membrane would lose its infinite selectivity due to significant crack and pinhole formation through the Pd membrane. The critical temperature for the α-β phase transition of the Pd alloys is lower than the pure Pd. Thus, the utilization of the Pd alloy membranes would provide a wider range of operating temperatures. A well known example of a Pd alloy membrane, namely a Pd/Ag membrane does not experience any H₂ embrittlement at temperatures below 300°C in the H₂ environment. Furthermore, the intermetallic diffusion and leak formation could be problematic at temperatures higher than 550°C due to decreased permeation and selectivity respectively.

As shown in Figure 2, the non-isothermal membrane reactor model was simulated using a feed temperature range of 250-400°C in order to identify reaction conditions which could eventually give rise to process hazards. The maximum temperature in the reaction side was limited to 500°C. When the feed temperature was higher than 250°C (in the zone which is on the right side of line 11 of Figure 2 [a]), the reaction side temperature limit was exceeded. The intermetallic diffusion of the components of porous support into the Pd/Alloy layer would decrease permeation and cause leak formation at temperatures 500°C and higher. As a consequence of leak formation, the reacting gases other than H₂ can diffuse into the permeate side. The CO conversion levels would drop and the reaction side temperature would decrease due to the heat carried by the gases diffusing to the permeate side. If a pure Pd membrane is used, the low temperature at the reactor inlet would damage the membrane. Keeping the feed temperature at 300°C would be more beneficial and another way for reducing the reaction side temperature, such as a higher steam flow rate, needs to be employed.
Figure 2. Contour plots of [a] $T_{\text{Rxn,Max}}$ [b] $R_{\text{H}_2}$ and [c] $X_{\text{CO}}$ as a function of inlet feed flow rate and feed temperature at $P_{\text{Total,Rxn}} = 15$ atm, $P_{\text{Tube}} = 1$ atm, $\text{H}_2\text{O}:\text{CO} = 2$ and 100% $\rho_{\text{Bulk,max}}$.

No reaction was taking place at a feed temperature of 200°C for all flow rates as shown in Figure 2. Additionally, the feed temperature should not be higher than 250°C in order not to exceed the reaction side temperature limit. Attaining the performance target levels of $X_{\text{CO}} = 98\%$ and $R_{\text{H}_2} = 95\%$, becomes challenging due to the limited range of feed temperatures considered. As can be seen from Figure 2 [b] and [c], the target levels of $X_{\text{CO}} = 98\%$ and $R_{\text{H}_2} = 95\%$ were not achieved at feed flow rates as low as 2000sccm. Thus, the specific reaction conditions should be carefully examined to reach these levels of performance through an inherently safe process.

If the feed temperature exceeds the limit of 550°C (MORE - $T_{\text{Feed}}$) due to overheating of the feed stream in the pre-heater and stays at that temperature for long times, the membrane will be damaged and the permeance will consequently decrease. On the other hand, a decrease of the feed temperature (LESS - $T_{\text{Feed}}$) will lead to deterioration in membrane performance by reducing the CO conversion and $\text{H}_2$ production rates. In addition to low productivity caused by the decreased feed temperature, pure Pd membranes can experience $\text{H}_2$ embrittlement. The temperature of the pre-heater should be monitored and the feed streams that are at an undesirable temperature level should be redirected through a backup line.

The non-isothermal membrane reactor model was also simulated under a wide range of feed flow rates (600-6000sccm) in order to highlight the competing effects between residence time and
reaction/permeation rate on process performance enhancement. An unplanned increase or decrease of the above process variable, depending on the extent of this change, could drive the process to undesirable operation conditions. In particular, an increase of the total feed flow rate (MORE-FFeed) can be caused by a malfunction of the flow control instruments, inappropriate adjustment and/or failure of the valves and pressure regulators. Furthermore, the Damköhler number (Da) which is the ratio of the maximum reaction rate to the space velocity is a good parameter to characterize and assess the consequences of such an increase of the total feed flow rate. Notice that depending on the extent of the increase of the feed flow rate two different cases: Da>1 or Da>>1 could be considered. When the unexpected increase of the total feed flow rate is not drastic, Da>1, the contact time with the catalyst would be enough to convert the reactants with the same conversions before the occurrence of the process excursion from the original operating conditions, however, since more CO is converted, the heat produced by reaction becomes also higher. The CO conversion and H₂ recovery may not be reduced but hot spots can cause membrane damage and catalyst sintering. If Da is much higher than 1, Da>>1, the space velocity increases and the residence time decreases. The efficiency of both of the isothermal and non-isothermal membrane reactors, CO conversion and H₂ recovery, can deteriorate due to lower residence times. Finally, the maintenance and inspection of the control instrument, valves and pressure regulators should be done on a regular basis. A backup line for the wet syngas feed has to be positioned before the entrance of the reactor and the feed has to be switched to inert gas in cases where the relief valve is used.

In addition to a malfunction possibility of the flow control instruments, inappropriate adjustment and/or failure of the valves and pressure regulators, as well as plugging of the lines which are located before the membrane reactor and any leaks on the feed line can result in a decrease (LESS-FFeed) in the total feed flow rate. As the feed flow rate decreases, the value of Da gets lower than 1. Two scenarios might be evaluated in the case of a decrease of the total feed flow rate: Da<1 or Da<<1, depending on the extent of the decrease. In the case of a moderate decrease of the feed flow rate, Da<1, the heat carried by the convective flow will be reduced but the process would not be affected significantly. If the total feed flow rate approaches an extremely low value leading to Da<<1, the reaction side temperature would decrease due to the decreased heat of reaction since less reactant is converted. Notice that the H₂ production rate of the isothermal membrane reactor and both the CO conversion and H₂ production rates of the non-isothermal membrane reactor will decline due to the lower feed flow rate. The temperature controller of the isothermal reactor has to act fast and the feed temperature of the non-isothermal reactor has to be maintained constant (at 300°C) to prevent a temperature drop inside the reactor. If the reason of the decreased flow is plugging of the lines or leakage, pressure may build up. A steady reliable operation of the filtration units has to be maintained to prevent plugging. An extra feed line needs to be added to the system in case of plugging to sustain the continuous operation of the process. In the case of leakage, poisonous gas detectors have to be positioned at multiple locations of the reaction and permeate sides of the reactor and an inert gas purge system should be built for the removal of potentially hazardous gases from the reactor unit until the source of the leak is identified and reparations are carried out. Similar reasons that could cause a decrease in the feed flow rate might lead to the worse case scenario of no flow (NO-FFeed). The surface of the Pd-based membrane might then be oxidized by the air in the pipeline, and therefore, it needs to be regenerated with H₂ prior to reaction.

3.1.2 Effect of bulk catalyst density

The forward reaction rate and also the heat produced by the exothermic WGS reaction are higher in the catalytic zone close to the membrane surface where the permeation rate is fastest. Hot spot formation on the membrane surface due to the fast forward reaction could damage the Pd
membrane and also sinter the catalyst. Diluting the catalyst mass with an inert packing would not only help to prevent the formation of hazardous hot spots but also would reduce the cost of the membrane reactor. Thus, the maximum temperature in the reaction side, overall CO conversion and H\textsubscript{2} recovery of the membrane reactor were calculated at a feed flow rate range of 600-6000 sccm and 2-100\% of the maximum bulk catalyst density. The reduction of the bulk catalyst density by distributing the catalyst weight evenly along the entire reactor length was not an effective way of decreasing the reaction side temperature. The maximum temperature in the reaction side remained at 530°C for all of the bulk catalyst density values at almost all feed flow rates as shown in Figure 3 [a]. Moreover, the performance indicators, X\textsubscript{CO} and R\textsubscript{H2}, were not significantly affected at the feed flow rates considered and by ρ\textsubscript{Bulk} values higher than 50\% of the ρ\textsubscript{Bulk,max}. Thus, packing the non-isothermal membrane reactor with 50\% of the ρ\textsubscript{Bulk,max} was selected for the ensuing simulation runs.

![Figure 3](image-url)

Figure 3. Contour plots of [a] T\textsubscript{Rxn,Max} [b] R\textsubscript{H2} and [c] X\textsubscript{CO} as a function of inlet feed flow rate and bulk catalyst density at T\textsubscript{Feed} = °C, 300 P\textsubscript{Total-Rxn} = 15 atm, P\textsubscript{Tube} = 1 atm, H\textsubscript{2}O:CO = 2.

3.1.3 Effect of H\textsubscript{2}O:CO mole ratio

The temperature rise due to the heat of reaction can easily cause the reaction side temperature to exceed the temperature limit of 500°C at feed temperatures above 300°C. Feed temperatures below 300°C reduce the permeation and forward reaction rates. Also, H\textsubscript{2} embrittlement remains a problem for pure palladium membranes below 300°C. While the feed
temperature is kept at 300°C and higher, the reaction side temperature needs to be lower than 500°C to protect the membrane. An effective way of reducing the reaction side temperature would be feeding excess steam to make use of the high latent heat of steam. Even though the heating cost of steam would be high, the utilization of excess steam to prevent high temperature zones for the safety of the operation of the Pd-Based membrane reactor is more crucial. Moreover, the increased steam flow rate would shift the WGS reaction to the products side and increase reaction yield along with the removal of H₂.

In the simulation runs, the total feed flow rate range was kept constant and the mole ratio of H₂O:CO was changed from 1 to 8 in Figure 3. The mole ratio of H₂O:CO should be higher than 3 to avoid exceeding the reaction side temperature limit of 500°C as presented in Figure 3 [a]. The temperature rise was not at acceptable levels for all feed flow rates considered, particularly at H₂O:CO ≤ 2 and the high temperature zones could undermine process safety by causing leak formation and an undesirable productivity decline by reducing the permeance due to intermetallic diffusion. Even though an 98% CO conversion was attained with H₂O:CO = 4 in Figure 4 [c], the H₂ recovery was as low as 80% at the corresponding conditions of Figure 4 [b]. The maximum of the H₂ recovery (88%) was observed with H₂O:CO = 2 because of the high residence time and temperature at this zone.

Figure 4. Contour plots of [a] T_{Rxn,Max} [b] R_{H2} and [c] X_{CO} as a function of inlet feed flow rate and the mole ratio of H₂O:CO at T_{Feed} = 300°C, P_{Total,Rxn} = 15 atm, P_{Tube} = 1 atm, 50% ρ_{Bulk,max}
Besides the apparent advantages of using excess steam such as decreased reaction side temperatures and shift of reaction to the products side, excess steam could prevent coke formation on the catalyst and/or Pd-Based membrane. If the dry syngas composition and flow rate at the outlet of the scrubber of the gasifier is assumed constant, the variable which can affect the composition of the wet syngas is the steam flow rate at the entrance of the reactor. Notice that possible deviations in the ratio of H₂O:CO might be caused by an error in the ratio controller. An increase of the H₂O:CO ratio (MORE- F\textsubscript{H₂O}) which is accompanied by an increase of the total feed flow rate, reduces the productivity of the process as mentioned earlier. The decrease of the residence time and reaction side temperature below the threshold limits due to an increase in the H₂O flow rate are the main reasons for the deviations from the desired product specifications observed. If the extent of the decrease of the H₂O:CO ratio (LESS- F\textsubscript{H₂O}) is drastic, lower than 1, the membrane reactor performance decreases due to lower CO conversion and H₂ production rates. Moreover, the H₂O:CO ratio has to be kept at 3 and higher to protect the non-isothermal membrane from hot spots. If precautions are not taken on time, the problem of reduced steam flow rate can get worse such as a potential failure of a water pump and may end up generating a situation of no steam flow (NO- F\textsubscript{H₂O}). The decreased H₂O:CO ratio and no steam flow conditions can cause coke formation on both of the catalyst and the membrane surface. In addition, plugging of the pipelines and/or the membrane reactor with the accumulation of deposited coke will eventually cause a pressure built up which is a serious safety concern. Relief valves need to be placed at various locations to decrease the system pressure in case of a pressure built up. Finally, the Fe-Cr based high temperature water gas shift catalyst and the Pd-based membrane have to be regenerated with steam before the process reverts to normal operation.

3.1.4 Effect of reaction side total pressure

Since the temperature rise in the reaction zone can be eliminated by using excess steam, other parameters such as reaction and permeate side pressure could be in principle used to enhance H₂ recovery levels while inducing a temperature profile in compliance with process safety limits/standards. Unlike the traditional packed bed reactors, the reaction side pressure could have a dramatic effect on the performance of a Pd-based water gas shift membrane reactor. Low levels of R\textsubscript{H₂} and production rate of pure H₂ could be enhanced by increasing the reaction side total pressure thus increasing the driving force for H₂ permeation.

The bulk catalyst density and H₂O:CO ratio were set at 50% of the ρ\textsubscript{bulk,max} and 4, respectively. The non-isothermal membrane reactor’s performance was evaluated under a reaction side total pressure range of 10-70 atm. Even though a wide range of reaction side total pressures (10-70 atm) was considered in the simulation runs conducted, the difference in the maximum temperature of the reaction side for all pressure values did not exceed 8°C as shown Figure 5 [a]. Furthermore, the maximum of the reaction side temperature was kept at 470-477°C with the aid of excess steam. It should be noted that operating at a lower temperature than the limit of 500°C would provide the required time to take action to control the process in case of any unexpected disturbances upsetting the process system under consideration. Performance target levels of X\textsubscript{CO} = 98% and R\textsubscript{H₂} = 95% were attained at a reaction side pressure of 45 atm and higher by using H₂O:CO =4 as depicted in Figure 5 [b] and [c]. Also, the membrane reactor’s operation remained practically unaffected under feed flow rates within the range of 600-6000scm as the reaction side pressure increased. However, there is no available information about how the thin (5-10µm) Pd-Based membrane reactors would behave at industrially relevant conditions for higher amounts of pure H₂ production. The high pressure at the reaction side might damage the thin Pd layer on the porous substrate. If the membrane is damaged under the effect of a high reaction side pressure,
reactants through the permeate side could reduce conversion, purity of the permeate side and even the reaction side pressure can drop significantly.

Figure 5. Contour plots of [a] $T_{\text{Rxn,Max}}$ [b] $R_{\text{H}_2}$ and [c] $X_{\text{CO}}$ as a function of inlet feed flow rate and the reaction side total pressure at $T_{\text{Feed}} = 300^\circ\text{C}$, $P_{\text{Tube}} = 1$ atm, $\text{H}_2\text{O}:\text{CO} = 4$ and 50% $\rho_{\text{Bulk,max}}$.

Drastic deviations associated with the reaction side total pressure, for example an increase (MORE – $P_{\text{Total,Rxn}}$), might arise from a possible malfunction of the compressor and back pressure regulators, plugging or closing of the valves as well as connections at the zones after the membrane exit. The higher $\text{H}_2$ partial pressure leads to an increase of the driving force and $\text{H}_2$ permeation rate. Consequently, CO conversion increases while more heat is released from the exothermic water gas shift reaction. The increased heat of reaction at high system pressures might cause the reaction temperature to exceed the temperature limit of the non-isothermal reactor. As already pointed out, the most effective way of reducing the temperature in the reaction side was shown to be an increase in the steam flow rate. In such a case, the steam flow rate can be increased gradually until the system pressure returns to its desired value. The rate of temperature rise especially at the reactor inlet might be faster than the speed of action of the temperature controller for the isothermal membrane reactor. In that case, hot spots might be a potential hazard for membrane integrity. Relief valves should be used to avoid over-pressure incidences and alarm systems need to be set up to warn the employees in the case of an adverse pressure increase. Similar to the reasons of the increase of the reaction side total pressure, a possible failure of the compressor and back pressure regulators, plugging or closing of the valves and connections at the zones before the membrane entrance, as well as leakage and defects on the membrane can result in a decrease of the reaction...
side total pressure (LESS – $P_{\text{Total,Rxn}}$). Reduced system pressure could affect the H$_2$ recovery of the membrane reactor drastically. Finally, notice that the production rate of pure H$_2$ decreases due to the reduced H$_2$ driving force and the pressure controllers employed have to respond fast to keep process productivity at the desired target levels.

3.1.5 Effect of permeate side pressure

As the driving force responsible for H$_2$ permeation is increased, the H$_2$ recovery and also CO conversion levels can be enhanced. The driving force for H$_2$ permeation can be increased by several ways such as through an increase in the reaction side pressure and the application of sweep gas or vacuum on the permeate side. In the present study neither the application of a sweep gas nor vacuum was considered. An extra separation unit would be necessary at the permeate side exit when a sweep gas is used. Moreover, the application of vacuum or using steam as the sweep gas might not be favorable in terms of energy consumption. However, the feasibility of the vacuum or sweep gas on the permeate side of the membrane reactor needs to be investigated through a detailed process economic analysis.

Application of vacuum on the permeate side was evaluated in this case to obtain directly pure H$_2$ without additional time and material requirements related to the use of a separation unit. The main goal was to mitigate the occurrence of any hazardous conditions in cases of high reaction side pressures while maintaining high performance target levels of $X_{\text{CO}} = 98\%$ and $R_{\text{H}_2} = 95\%$. In particular, the reaction side pressure was kept at a moderately low pressure of 20 atm and the permeate side pressure was changed to fall within the range of 0.1-1 atm with the application of vacuum. The performance target levels can easily be attained by applying vacuum on the permeate side without a significant temperature rise in the reaction side as shown in Figure 6 [a]. The difference in the maximum temperature in the reaction side was not higher than 3°C. If the permeate side H$_2$ pressure can be reduced to 0.2 atm, complete CO conversion and very high H$_2$ recovery can be achieved as depicted in Figure 6 [b] and [c]. However, strict caution needs to be exercised to maintain the H$_2$O:CO ratio of 4 and higher and thus keep the reaction side temperature below the maximum temperature limit. As shown in Figure 6 [b] and [c], the original performance target levels of $X_{\text{CO}} = 98\%$ and $R_{\text{H}_2} = 95\%$ were achieved at a permeate side H$_2$ pressure and reaction side total pressure of 0.4 atm and 20 atm respectively.
3.1.6 Effect of impurities in the feed stream

A possible malfunction of the gas cleaning unit located before the membrane reactor could produce unacceptable levels of impurities. Pure Pd and Pd-Alloy membranes lose their high permeance values partly or completely in the presence of impurities such as H$_2$S in the feed stream (MORE-F$_{\text{Impurity}}$). The formation of Pd$_4$S at 320°C with a concentration of 20 ppm H$_2$S/H$_2$ was observed in Pd foil experiments $^{34}$. Micro-defects may form on the pure palladium surface due to changes in the lattice parameter and membrane selectivity declines when Pd$_4$S is formed $^{35, 36}$. Therefore, if a pure palladium membrane is utilized in the reactor and the feed steam is not H$_2$S free, membrane selectivity and H$_2$ purity of the permeate flow could decrease significantly. Chen and Ma $^{37}$ showed that after exposure of a pure palladium membrane to a 54.8 ppm H$_2$S/H$_2$ mixture, no permeance recovery was possible due to the irreversible formation of bulk Pd$_4$S. As a result, the replacement of the poisoned pure palladium membrane is necessary to maintain high productivity levels of the process. Pd-Alloy membranes, particularly Pd-Au and Pd-Cu, have the advantages of recovery and selectivity stability of the Pd-based membrane after poisoning $^{37, 38}$. Membrane reactors, in which Pd-Au and Pd-Cu membranes are utilized should be regenerated with H$_2$ after exposure to H$_2$S to increase the permeance of the membrane. Finally, placement of the gas composition analyzers at the entrance of the membrane reactor and at the exit of the permeate side is crucial in order to take fast action and prevent potential poisoning.
3.2 The membrane reactor under adiabatic conditions

If an adiabatic membrane reactor could be designed to induce a similar performance profile to that of the isothermal membrane reactor, the energy released from the exothermic water gas shift reaction could be utilized to heat the membrane reactor without the need for an extra heating source. However, Pd based membranes have a minimum and maximum working temperature and the consequences of any undesired drop or rise in the temperature need to be identified in advance in order to mitigate the risk associated with potentially hazardous incidents. Within such a context, a dynamic process model could be used to generate process safety-relevant scenarios and therefore elucidate the corresponding chains of causality linking root causes and consequential variations in key process variables to operational outcomes and performance levels. Parameters with a significant effect on reactor temperature such as the weight of loaded catalyst, feed temperature, \( \text{H}_2\text{O}:\text{CO} \) ratio of the feed and permeance of the membrane were considered and appropriately perturbed in all model simulation runs in order to remain within the acceptable temperature range of 300-500°C. The feed temperature and the initial reactor temperature were chosen at 300°C. The bulk catalyst density was reduced to a value of 40% of \( \rho_{\text{Bulk,max}} \) in order to have a gradual increase in the extent of the reaction instead of an immediate increase at the reactor inlet. Even though the permeation of \( \text{H}_2 \) from the reaction side caused a heat loss, the removal of the product \( \text{H}_2 \) increased the forward reaction rate and the temperature due to the exothermic reaction. Thus, the permeance was selected at 70% of the Pd foil with the same Pd thickness of 10 \( \mu \)m. It was observed that the \( \text{H}_2\text{O}:\text{CO} \) ratio had a strong effect on the reaction side temperature profile. When the value of the \( \text{H}_2\text{O}:\text{CO} \) ratio was selected at 2, the reaction side temperature could not be reduced lower than 577°C. Consequently, a \( \text{H}_2\text{O}:\text{CO} \) ratio of 4 was used in the model so that the maximum reaction side temperature stayed at 480°C with an overall \( \text{CO} \) conversion of 98% and \( \text{H}_2 \) recovery of 82%.

The dynamic behavior of the adiabatic membrane reactor during the start-up stage is shown in Figure 7. In particular, the dashed arrows show the direction of time progression from 0 to 100 minutes and the reaction side temperature profiles along the length of the reactor as functions of time are depicted in Figure 7 [a] showing that the adiabatic membrane reactor reached steady state conditions in about 100 minutes. The reaction side temperature profile as obtained from the unsteady state model when steady state was attained was then compared with the results of the first-principle based steady state model with no approximation under the same set of conditions (Blue dashed line in Figure 7). Notice that the result obtained from the unsteady state model under the lumped parameter approximation deviates approximately 10 °C from the one offered by the steady state model. Unlike the reaction side temperature, the streams of each reacting component reached the reactor exit and also attained their respective steady state values faster as shown in Figure 7 [b]. In particular, the \( \text{CO} \) stream reached the reactor exit in about 5 seconds and the corresponding steady state was reached in 25 minutes. The \( \text{CO} \) conversion and \( \text{H}_2 \) recovery profiles along the length of the reactor at steady state in Figure 7 [c] showed that even a 40% reduction of the Pd membrane area would not significantly affect the values of \( X_{\text{CO}} \) and \( R_{\text{H}_2} \).
Figure 7. [a] The reaction side temperature and [c] CO molar flow rate profiles along the length of the reactor during the start-up of the adiabatic membrane reactor. [c] The $X_{CO}$ and $R_{H2}$ profiles at the steady state conditions. $T_{Feed} = 300 \, ^\circ C$, $P_{Total,Rxn} = 15 \, atm$ and 40% of $\rho_{Bulk,max}$.

4. Conclusions

A standard Hazard and Operability (HAZOP) analysis was pursued to identify potential hazards as well as failure modes and hopefully prevent potential risks to personnel, environment, equipment and/or process efficiency and performance. In particular, the effect of variations (random or intentional) in the total feed flow rate and temperature, catalyst loading, $H_2O:CO$ ratio, reaction and permeate side pressures and purity of the feed on the process state in the form of possibly adverse process excursions/deviations from normal operating conditions was considered as part of a process safety analysis protocol associated with Pd-based membrane reactors. The absence of adequate control of the reactor temperature as well as the purity of the feed which may cause hot spots and decline in the permeance and selectivity were identified and classified as critical for the operation of the WGS membrane reactor. Utilization of excess steam together with the application of vacuum on the permeate side was found to be the most effective method of reducing the temperature rise in the reaction zone without decreasing the overall CO conversion and H$_2$ recovery. If the suggested precautionary measures are taken by considering the possible consequences of the aforementioned deviations in the operating conditions as identified through the proposed membrane reactor modeling framework, the membrane reactor could be operated safely without compromising the high performance target levels of 98% CO conversion and 95% extra pure (99.9999%) H$_2$ recovery.
Acknowledgements

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Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>surface or cross sectional area (m²)</td>
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<tr>
<td>C</td>
<td>concentration (mol/m³)</td>
</tr>
<tr>
<td>Cₚ</td>
<td>molar heat capacity at constant pressure (J/mol.K)</td>
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<tr>
<td>E</td>
<td>activation energy (J/mol)</td>
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<td>f</td>
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<td>F</td>
<td>molar flow rate (mol/s)</td>
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<td>H</td>
<td>enthalpy (J/mol)</td>
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<tr>
<td>J</td>
<td>flux (mol/m².S)</td>
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<tr>
<td>O.D.</td>
<td>outside diameter of the tube</td>
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<tr>
<td>I.D.</td>
<td>inside diameter of the shell</td>
</tr>
<tr>
<td>l</td>
<td>Pd thickness of the membrane (μm)</td>
</tr>
<tr>
<td>L</td>
<td>length (m)</td>
</tr>
<tr>
<td>n</td>
<td>number of moles (mol)</td>
</tr>
<tr>
<td>N</td>
<td>total number of lumps/segments</td>
</tr>
<tr>
<td>P</td>
<td>pressure (Pa)</td>
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<tr>
<td>R_H₂</td>
<td>hydrogen recovery (%)</td>
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<tr>
<td>r</td>
<td>reaction rate (mol/[kg cat. s])</td>
</tr>
<tr>
<td>Q</td>
<td>permeability of the membrane (mol H₂.μm/[m². s. atm⁰.⁵])</td>
</tr>
<tr>
<td>Q₀</td>
<td>permeability constant of the membrane (mol H₂.μm/[m². s. atm⁰.⁵])</td>
</tr>
<tr>
<td>t</td>
<td>time (s)</td>
</tr>
<tr>
<td>T</td>
<td>temperature (K)</td>
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<tr>
<td>U</td>
<td>overall heat transfer coefficient (W/[m².K])</td>
</tr>
<tr>
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<tr>
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<td>cumulative weight of catalyst (kg)</td>
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<td>spatial coordinate (m)</td>
</tr>
<tr>
<td>Z</td>
<td>dimensionless spatial coordinate (y/L)</td>
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Greek symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>∆v</td>
<td>volume of each segment (m³)</td>
</tr>
</tbody>
</table>
\( \Delta w \) : weight of catalyst for each segment (g)

\( \Delta y \) : length of each segment (m)

\( \varepsilon \) : void fraction of the catalytic bed

\( \rho \) : density \((\text{kg/m}^3)\) \(\rho_{\text{Bulk, max}}\) : weight of catalyst required to fill the annular space without inert packing/annular reactor volume

**Subscripts**

Annulus: the annular space between the shell casing and membrane

\( c \) : cross section

\( i \) : \( i \)th species

\( m \) : membrane

Rxn : reaction

**Superscripts**

shell : shell side of the membrane module where reaction is taking place (Reaction side)

tube : tube side of the membrane module where permeated H₂ is flowing through (Permeate side)

References


