

Simulation of Water Gas Shift Zeolite Membrane Reactor

I G B N Makertiharta, Z Rizki, Megawati Zunita and P T Dharmawijaya

Chemical Engineering Department, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung, West Java, 40132, Indonesia

E-mail: megazunita.105@gmail.com

Abstract. The search of alternative energy sources keeps growing from time to time. Various alternatives have been introduced to reduce the use of fossil fuel, including hydrogen. Many pathways can be used to produce hydrogen. Among all of those, the Water Gas Shift (WGS) reaction is the most common pathway to produce high purity hydrogen. The WGS technique faces a downstream processing challenge due to the removal hydrogen from the product stream itself since it contains a mixture of hydrogen, carbon dioxide and also the excess reactants. An integrated process using zeolite membrane reactor has been introduced to improve the performance of the process by selectively separate the hydrogen whilst boosting the conversion. Furthermore, the zeolite membrane reactor can be further improved via optimizing the process condition. This paper discusses the simulation of Zeolite Membrane Water Gas Shift Reactor (ZMWGSR) with variation of process condition to achieve an optimum performance. The simulation can be simulated into two consecutive mechanisms, the reaction prior to the permeation of gases through the zeolite membrane. This paper is focused on the optimization of the process parameters (e.g. temperature, initial concentration) and also membrane properties (e.g. pore size) to achieve an optimum product specification (concentration, purity).

1. Introduction

At the present, a lot of researchers focus on searching alternative renewable energy sources. Hydrogen becomes one of the potential subjects. Hydrogen as an energy source took the attention of many researchers due to its ease of obtaining yet simple production process, as well as zero pollution emissions [1]. This condition then challenges researchers to continuously improve the effectiveness and efficiency of the hydrogen production process.

The water gas shift (WGS) reaction is used widely in industry. Commonly, this process is performed in two consecutive stages to achieve both fast reaction kinetics and high conversion. High temperature (300 - 450°C) reactions is performed prior to low temperature (150 - 300°C) one [2, 3]. Due to the exothermic reaction, the low temperature condition may increase the conversion. This conventional operation has major drawbacks related to the two steps complex operation, large catalyst consumption and high steam recycling.

Improving the hydrogen production via WGS reaction can be performed by integrating the reactor with the membrane separation process resulting the membrane reactor [4, 5]. The research of integrative process which focused on reactor using hydrogen selective membrane has been considered as an alternative strategy for process optimization [6, 7].

The membrane that is used for WGS reaction requires some important properties including the thermal stability, good hydrogen permeability, stable against chemical and also highly selective for



hydrogen. Researchers reported that those properties can be found in zeolite [8-10] which makes the Zeolite Membrane Water Gas Shift Reactor (ZMWGSR) an interesting topic to be investigated further. In that scheme, the hydrogen produced inside the reactor will be directly separated from other gases in the stream [11, 12], which can be seen in **Error! Reference source not found.**

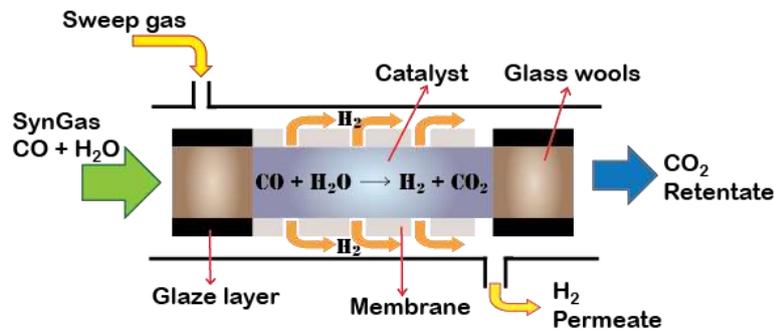


Figure 1. Scheme of Tubular Membrane Reactor for WGS Reaction.

As in many other reactors, a catalyst in WGS reactor is a key-point to achieve a good reactor performance [13]. Current development for research concerning WGS reaction is by directly combining both catalyst and H₂ separator. Conventionally, Pd, Fe-Cr oxides catalyst are used in WGS reaction which operates at temperature above 40°C [1, 3, 4].

This paper studies a simulation approach of ZMWGSR which more focus on the reaction conditions. The variables studied includes CO/H₂O ratio, pressure and temperature while specifically observed the effects on hydrogen recovery and separation factor.

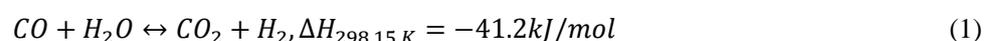
2. Zeolite membrane reactor for water gas shift reaction

For years, researchers have been working on the development of ZMWGSR. The zeolite itself has specific characters regarding to its pore size and structure that can be utilized in certain purpose. Moreover, zeolite is also more stable in high temperature which makes it suitable for WGS reactor. Several researchers have performed modification method to increase the hydrogen production [12, 14]. Typical zeolite used in ZMWGSR are the MFI (ZSM-5 or silicate-1) (diameter 0,53 x 0,56 nm) and DDR (deca-dodecasil 3R) (diameter 0,46 x 0,44) [15, 16]. The MFI zeolite has given a new outlook in high temperature hydrogen production using WGS reaction. However, the MFI zeolite still has a very large pore size thus the permeance is high with low selectivity [17]. Therefore, Masuda et al [18] modified the zeolite membrane using silane to reduce the pore size.

Previous studies mentioned that the MFI type zeolite reactors could not be directly used for WGS performance prediction because the difference in permeation and separation mechanism [15, 17, 18]. Hence, this paper studies the influence of some parameters such as pressure, temperature effect, CO/H₂O ratio to the performance of zeolite membrane reactor in WGS. Practically, WGS zeolite membrane reactor is operated at high pressure about 20 atm. However, the effect of operation pressure, temperature effect, CO/H₂O ratio on WGS reaction in a tubular zeolite membrane is still not clear.

3. Reaction and permeation model

WGS reaction is an exothermic reaction which conversion is limited by the equilibrium condition, see equation ((1)). In this simulation, some parameters were set in the range of commonly used value which have been reported. The operating condition used in this simulation is shown in Table 1.



The kinetic of WGS reaction had been modelled using various equation. More specifically, the empirical power-law model is the most common one due to its simplicity yet effective. In this paper, a

kinetic model using Fe-Cr-Cu catalyst developed by Hla et al. [1] is used. The power law model in such condition is shown by equation (2).

$$r_A = 10^{0.659} \exp\left(\frac{-8.8 \times 10^4}{RT}\right) P_{CO}^{0.9} P_{H_2O}^{0.31} P_{CO_2}^{-0.156} P_{H_2}^{-0.05} \left(1 - \frac{1}{K_{eq}} \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}\right) \quad (2)$$

Where r_A is the reaction rate ($\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$), R is the gas constant, T is the temperature (K), P_i is the partial pressure of component i in the reaction zone (Pa). K_{eq} is the temperature-dependent thermodynamic equilibrium constant for WGS, which can be defined as [19]:

$$\ln(K_{eq}) = \frac{5693.5}{T} + 1.077 \ln(T) + 5.44 \times 10^{-4} T - 1.125 \times 10^{-7} T^2 - \frac{49170}{T^2} - 13.148 \quad (3)$$

Besides the reaction model, a permeation model needed to be considered in this simulation. This paper used the gas translational diffusion model proposed to predict diffusivity in zeolite pores for small gases diffusion with weak adsorption affinity with zeolite [20]. The permeance of each gas component in reaction mixture (H_2O , CO , H_2 , CO_2 , and Ar) can be expressed as [21]:

Permeation model of zeolite membrane in this paper used the gas translational diffusion model proposed to predict diffusivity in zeolite pores for small gases diffusion with weak adsorption affinity with zeolite [20]. The permeance of each gas component in reaction mixture (H_2O , CO , H_2 , CO_2 , and Ar) can be expressed as [21]:

$$j_i = \frac{\varphi \alpha}{\delta \lambda} \left(\frac{8}{\pi R T M_i}\right)^{1/2} \exp\left(\frac{-E_{d,i}}{RT}\right) \quad (4)$$

Where j_i is the permeance of component i through the membrane ($\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$), φ is the membrane porosity (~ 0.25) to tortuosity ratio, which for MFI membrane has the value of 0.05 [22], δ is the thickness of the membrane (m). α is the diffusion length or distance between two adjacent sites (m), which is about 1 nm for diffusion in MFI zeolite [22], k is the diffusion coordination number (4 for MFI), M_i is the molecular weight of the diffusing gas (g mol^{-1}), $E_{d,i}$ is the activation energy for diffusion of the gas i in the micropores (kJ mol^{-1}), which is determined by the relative size of diffusing gas molecule to the zeolite pore size. Typical values of $E_{d,i}$ are 13.39, 13.14, 12.55, and 14.97 kJ mol^{-1} for H_2 , CO , CO_2 and Ar , respectively [17].

Table 1. WGS Membrane Reaction Condition

Parameters	Value
Temperature Range ($^{\circ}\text{C}$)	400-600
Feed inlet/outlet pressure ($\times 10^5$ Pa)	5 – 25
Permeate pressure ($\times 10^5$ Pa)	1
Feed $\text{H}_2\text{O}/\text{CO}$ ratio ($R_{\text{H}_2\text{O}/\text{CO}}$) (mol/mol)	0.33 – 3
Volumetric flow rate	$1.1 - 5.5 \times 10^{-7}$
Ar sweeping flow rate ($\text{m}^3(\text{STP})/\text{s}$)	$1.1 - 5.5 \times 10^{-7}$
Fe/Ce catalyst (mg)	200
Inner Radial (m)	3.5×10^{-3}
Membrane thickness (m)	3×10^{-6}
Membrane length (m)	1.5×10^{-2}

4. Membrane reactor model

The model for membrane reactor was constructed based on the mass balance equations assuming the ideal gas behavior. The zone inside the reactor was categorized into two, inside the tube where the

reaction occurs and at the shell side. The partial pressure profile for each component in both zone is expressed in equation (5) (tube side) and (6) (shell side). The i index indicates the component inside the tube while the j indicates the component at the shell side. The axial and radial position inside the reactor are annotated with z and r . R , T , and Q indicate the gas constant, isothermal process temperature and volumetric flow rate respectively. ρ_B is the packing density in the reactor and ν is the stoichiometric coefficient. It was reported that the selectivity of H_2/H_2O was very low [23] resulting a negligible value of permeation. Thus, the water permeance was excluded in this simulation.

$$\frac{dP_i}{dz} = \frac{R \cdot T}{Q} \pi r^2 \rho_B \nu_i r_A - 2\pi r j_i \Delta P_i \quad (5)$$

$$\frac{dP_j}{dz} = \frac{R \cdot T}{Q} 2\pi r j_j \Delta P_j \quad (6)$$

Equation 5 and 6 expressed the performance of ZMWGSR. Those equations would show a conventional WGS reactor behavior when the permeance (j_i) was set to be zero. Those equations are the differential equation which need to be solved simultaneously. Considering the components at the tube and shell side, there are 9 differential equations that need to be solved simultaneously. Those equations are solved using numerical method via Matlab[®].

The performance of the membrane reactor is indicated by the CO conversion and the Hydrogen recovery which calculated via these equations.

$$X_{CO} = \frac{F_{CO}^{tube\ in} - F_{CO}^{tube\ out} - F_{CO}^{shell\ out}}{F_{CO}^{feed\ in}} \quad (7)$$

$$R_{H_2} = \frac{F_{H_2}^{shell\ out}}{F_{H_2}^{tube\ out} + F_{H_2}^{shell\ out}} \quad (8)$$

5. Results and discussion

5.1. Partial pressure profile

Each component in the conventional WGS reactor gives a sudden change in partial pressure which indicates a rapid reaction. Compared to the mass transport of each gas involved, the kinetic reaction is much higher which is typical for WGS reaction. Afterward, the partial pressure remains constant along the reactor since the equilibrium has been reached instantly. In a ZMWGSR, permeation of gases is expected. In the simulation, a decline of gases' partial pressure is observed. However, this kind of behavior is only appeared at low volumetric rate. As the inlet volumetric rate increase from $3,3 \times 10^{-8}$ to $3,3 \times 10^{-5}$ the partial pressure profile of each component along the ZMWGSR becomes similar with the conventional WGS reactor. This indicates that the mass transfer of the gases, especially hydrogen, through the membrane occurs slowly. Furthermore, the high flow rate also gives a flushed effect resulting more hydrogen flushed away with the stream resulting low recovery (Fig3). In term of CO conversion, a ZMWGS reactor shows a higher value while still affected by the volumetric rate. A relative increase of 9.2% is observed using volumetric rate of 3.3×10^{-8} m³/s while only 0,07% at 3.3×10^{-5} m³/s.

The reduction of partial pressure along the reactor at the ZMWGSR inside the tube is also followed by the increase of pressure at the shell side which indicates the transport phenomena occur. Figure 3 showed the partial pressure of each component at the shell side. It can be seen that the pressure of hydrogen is significantly higher than CO and CO₂. Moreover, the back flow of Argon as the sweep gas from the shell side is low. These indicate a good selectivity of zeolite to separate hydrogen from other gases involves in ZMWGSR system.

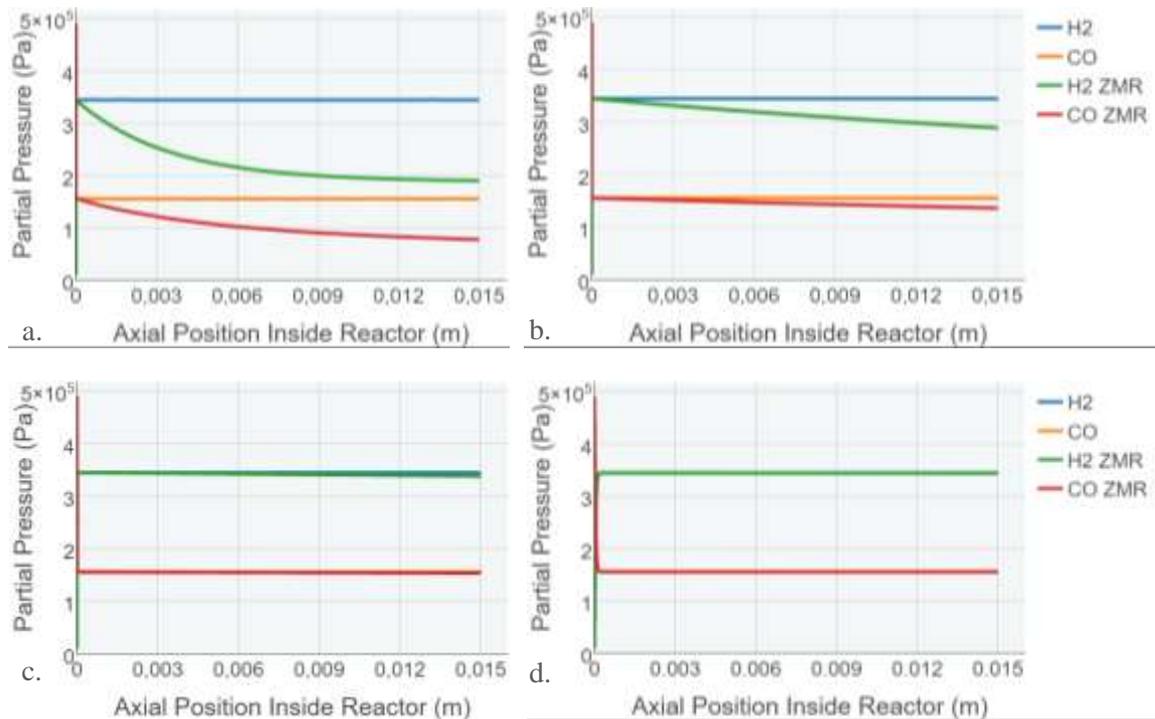


Figure 2. Partial Pressure of Hydrogen and CO inside the tube in Conventional WGS and ZMWGS Reactor with CO/H₂O ratio 1, Operating Pressure 10 bar, Operating Temperatur 500°C, Tube and Sweep Gas Volumetric Flow of a. 3.3×10^{-8} , b. 3.3×10^{-7} , c. 3.3×10^{-6} and d. 3.3×10^{-5} m³/s.

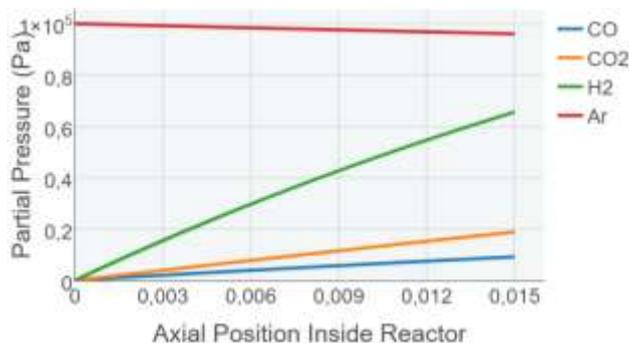


Figure 3. Partial Pressure Profile of Each Component at the Shell Side along the Reactor with CO/H₂O ratio 1, Operating Pressure 10 bar, Operating Temperature 500°C, Tube and Sweep Gas Volumetric Flow of 3.3×10^{-7} m³/s.

5.2. Molar ratio effect

In term of partial pressure, the best profile is observed at an equimolar flow of CO to steam (Fig 4). The hydrogen pressure at the shell side decreases as the carbon to steal decrease. This reduction is also observed while the carbon to steam ratio increases.

On the other hand, the conversion in a ZMWGSR is highly dependent in the CO to steam ratio with a negative correlation. The highest conversion is observed at low CO to steam ratio which correlates to simulations performed by other authors [24, 25].

However, this variation does not show a big effect in H₂/CO₂ separation factor and the hydrogen recovery. The separation factor shows the lowest value at equimolar feed composition. Meanwhile the increase up to 1/3 or 3/1 ratio is less than 0,1%. Furthermore, the change of reactants ratio does not give an effect to the hydrogen recovery. Thus, the amount of hydrogen removed in the shell side is still proportional to which in the tube side.

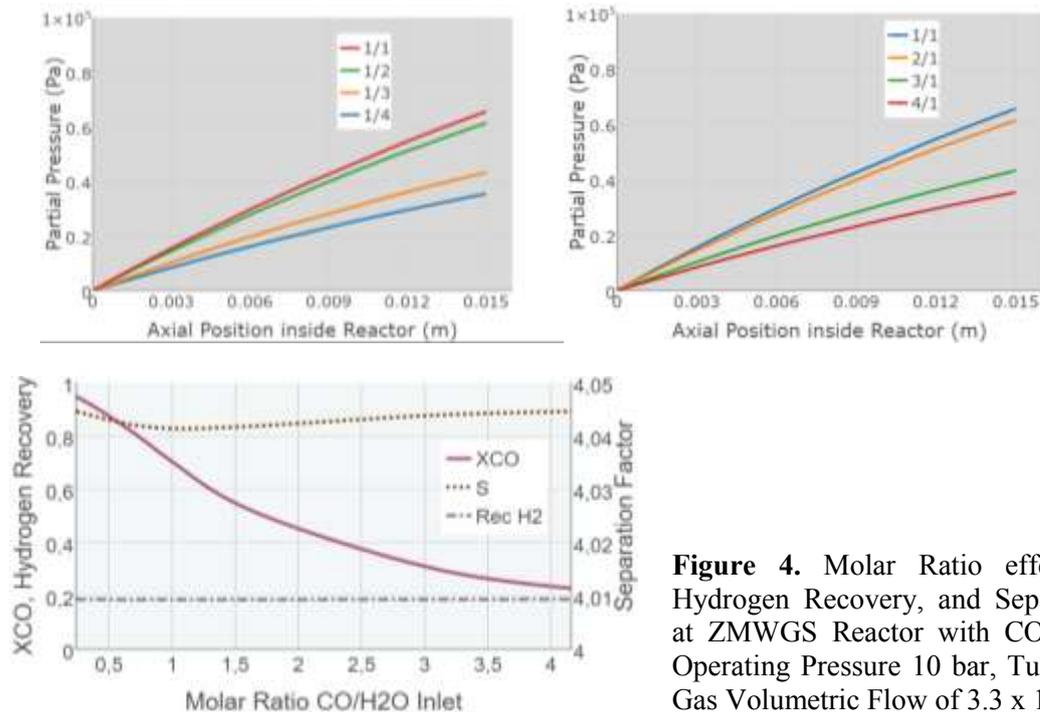


Figure 4. Molar Ratio effect to XCO, Hydrogen Recovery, and Separation Factor at ZMWGS Reactor with CO/H₂O ratio 1, Operating Pressure 10 bar, Tube and Sweep Gas Volumetric Flow of $3.3 \times 10^{-7} \text{ m}^3/\text{s}$.

5.3. Flow rate effect

The system in ZMWGSR consists of two streams, the one inside the tube and another one at the shell. Both streams may affect the performance of the ZMWGSR itself. It is explained at the previous section that the permeation from the tube to the shell side is better at low volumetric rate. Figure 5 shows that the partial pressure of hydrogen at the shell side is higher when low flow rate is applied. At higher flow rate, more hydrogen will be flushed away before it could even travel through the membrane. Thus, the hydrogen recovery value becomes lower. At the opposite, the separation factor shows a positive correlation with the inner tube flow rate. (Figure 6.a)

The flush effect also occurs at the sweep gas. However, the flushed hydrogen at the shell side gives a good effect in the ZMWGSR system. Thus, increase the hydrogen recovery. Figure 6.b shows that the increase in the sweep gas flow rate is followed by the increase of hydrogen recovery. Meanwhile, the other parameters are seemed to be not affected. Furthermore, high sweep gas flow rate cuts off the chance of Argon to permeate to the tube side. This means the loss of sweep gas becomes lower.

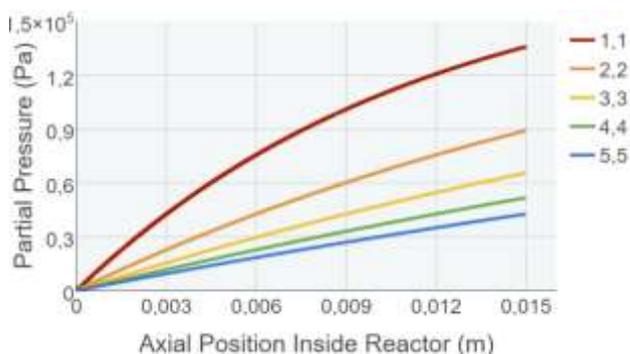


Figure 5. Hydrogen Partial Pressure Profile at the Shell Side along the Reactor with CO/H₂O ratio 1, Operating Pressure 10 bar, Operating Temperature 500⁰C, Sweep Gas Volumetric Flow of $3.3 \times 10^{-7} \text{ m}^3/\text{s}$, and the Inlet Tube Volumetric Flow ranges from 1.1 to $5.5 \times 10^{-7} \text{ m}^3/\text{s}$.

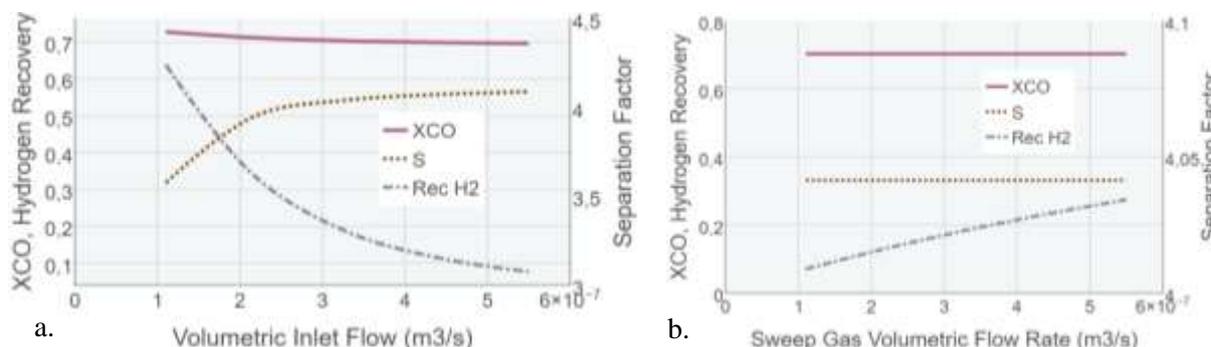


Figure 6. Effect of a. Inlet Tube and b. Sweep Gas Flow Rate to CO Conversion, Hydrogen Recovery and Separation Factor using CO/H₂O ratio 1, Operating Temperature 500⁰C and Operating Pressure 10 bar.

5.4. Pressure and temperature effect

The inlet pressure at the tube side increases the partial pressure of hydrogen at the shell side. This corresponds with the flux equation which is pressure dependent. Increase in tube side pressure will increase the pressure difference between the tube and shell, thus enhance the transfer across the membrane. However, this increase seems to be proportional thus does not significantly affect the hydrogen recovery.

In this simulation, the CO conversion for both membrane reactor and conventional reactor does not differ so much. Hence, the conversion decreases as the temperature increase. Moreover, the hydrogen recovery and separation factor is also observed to be temperature-dependent. The separation factor has a maximum value at 550⁰C, at a value of 4.045 while the hydrogen recovery has a positive correlation with temperature. A recovery of 0.23 is observed at 600⁰C while using CO to steam ratio 1, at 10 bar.

5.5. Process optimization

It is observed in this simulation that the performance of a ZMWGSR is more sensitive to CO/H₂O ratio and the tube inlet flow rate. The tube inlet flow rate affects hydrogen recovery and separation factor in a different way, thus an optimum condition for both parameters may apply. Such condition is reached at flow rate of 2,2 x 10⁻⁷ m³/s. The carbon to steam ratio gives the best performance at the lowest value the system can achieve.

The performance of a ZMWGSR may also affected by other parameters discussed in this paper. However, the effect is not as significant as the carbon to steam ratio and the inlet flow rate. The sweep gas flow rate improves the hydrogen recovery and potentially to be able for further increase outside the simulation range. However the cost of the sweep gas itself may be the constrain in increasing the sweep gas flow rate

6. Conclusion

A simulation of Zeolite Membrane Water Gas Shift (ZMWGS) reactor has been performed in this study. Integrating a zeolite membrane into a conventional WGS reactor increases the CO conversion. However the pressure profile across the ZMWGS reactor will be close to the conventional one when the flow rate is high.

This simulation also observes the effect of several operating parameters in the ZMWGSR performance. Parameters that affect the system significantly are found to be the carbon to steam ratio and the inlet flow rate. The optimum condition is achieved at flow rate of 2,2 x 10⁻⁷ m³/s and low carbon to steam ratio. The pressure gives effect to hydrogen partial pressure at the shell side yet not affecting the hydrogen recovery. The optimum temperature for this process is observed at 550⁰C.

7. References

- [1] Lee J Y, Lee D-W, Lee K-Y and Wang Y 2009 Cr-free Fe-based metal oxide catalysts for high temperature water gas shift reaction of fuel processor using LPG *Catal. Today* **146** 260-4.
- [2] Mendes D, Garcia H, Silva V, Mendes A and Madeira L M 2008 Comparison of nanosized gold-based and copper-based catalysts for the low-temperature water– gas shift reaction *Ind. Eng. Chem. Res.* **48** 430-9.
- [3] Bi Y, Xu H, Li W and Goldbach A 2009 Water–gas shift reaction in a Pd membrane reactor over Pt/Ce 0.6 Zr 0.4 O 2 catalyst *Int. J. Hydrogen Energy* **34** 2965-71.
- [4] Brunetti A, Caravella A, Fernandez E, Pacheco Tanaka D A, Gallucci F, Drioli E, Curcio E, Viviente J L and Barbieri G 2015 Syngas upgrading in a membrane reactor with thin Pd-alloy supported membrane *Int. J. Hydrogen Energy* **40** 10883-93.
- [5] Baker R W 2004 *Membrane Technology and Applications, Second Edition*, pp 393-423.
- [6] Ockwig N W and Nenoff T M 2007 Membranes for hydrogen separation *Chem. Rev.* **107** 4078-110.
- [7] Gallucci F, Fernandez E, Corengia P and van Sint Annaland M 2013 Recent advances on membranes and membrane reactors for hydrogen production *Chem. Eng. Sci.* **92** 40-66
- [8] Tavolaro A and Drioli E 1999 Zeolite membranes *Adv. Mater.* **11** 975-96.
- [9] Kim S-J, Yang S, Reddy G K, Smirniotis P and Dong J 2013 Zeolite membrane reactor for high-temperature water-gas shift reaction: effects of membrane properties and operating conditions *Energy Fuels* **27** 4471-80.
- [10] Basile A, Curcio S, Bagnato G, Liguori S, Jokar S M and Iulianelli A 2015 Water gas shift reaction in membrane reactors: Theoretical investigation by artificial neural networks model and experimental validation *Int. J. Hydrogen Energy* **40** 5897-906.
- [11] Chein R Y, Chen Y C and Chung J N 2015 Sweep gas flow effect on membrane reactor performance for hydrogen production from high-temperature water-gas shift reaction *J. Membr. Sci.* **475** 193-203.
- [12] Tang Z, Kim S-J, Reddy G K, Dong J and Smirniotis P 2010 Modified zeolite membrane reactor for high temperature water gas shift reaction *J. Membr. Sci.* **354** 114-22.
- [13] Ratnasamy C and Wagner J P 2009 Water gas shift catalysis *Catal. Rev.* **51** 325-440.
- [14] Hong M, Falconer J L and Noble R D 2005 Modification of zeolite membranes for H₂ separation by catalytic cracking of methyl-diethoxysilane *Ind. Eng. Chem. Res.* **44** 4035-41.
- [15] Gu X, Tang Z and Dong J 2008 On-stream modification of MFI zeolite membranes for enhancing hydrogen separation at high temperature *Microporous Mesoporous Mater.* **111** 441-8.
- [16] Wang H, Dong X and Lin Y S 2014 Highly stable bilayer MFI zeolite membranes for high temperature hydrogen separation *J. Membr. Sci.* **450** 425-32.
- [17] Tang Z, Dong J and Nenoff T M 2009 Internal surface modification of MFI-type zeolite membranes for high selectivity and high flux for hydrogen *Langmuir* **25** 4848-52.
- [18] Masuda T, Fukumoto N, Kitamura M, Mukai S R, Hashimoto K, Tanaka T and Funabiki T 2001 Modification of pore size of MFI-type zeolite by catalytic cracking of silane and application to preparation of H₂-separating zeolite membrane *Microporous Mesoporous Mater.* **48** 239-45.
- [19] Lima D F B, Zanella F A, Lenzi M K L and Ndiaye P M 2012 *Petrochemicals*, ed V Patel
- [20] Xiao J and Wei J 1992 Diffusion mechanism of hydrocarbons in zeolites—I. Theory *Chem. Eng. Sci.* **47** 1123-41.
- [21] Kanezashi M, O'Brien-Abraham J, Lin Y and Suzuki K 2008 Gas permeation through DDR-type zeolite membranes at high temperatures *AIChE J.* **54** 1478-86.
- [22] Kanezashi M and Lin Y 2009 Gas permeation and diffusion characteristics of MFI-type zeolite membranes at high temperatures *J. Phys. Chem. C* **113** 3767-74.
- [23] Dong T, Yu X, Miao C, Rasco B, Garcia-Pérez M, Sablani S S and Chen S 2015 Selective esterification to produce microalgal biodiesel and enrich polyunsaturated fatty acid using zeolite as a catalyst *RSC Adv.* **5** 84894-900.

- [24] Hla S S, Morpeth L D and Dolan M D 2015 Modelling and experimental studies of a water – gas shift catalytic membrane reactor *Chem. Eng. J.* **276** 289-302.
- [25] Dong X, Wang H, Rui Z and Lin Y S 2015 Tubular dual-layer MFI zeolite membrane reactor for hydrogen production via the WGS reaction : Experimental and modeling studies *Chem. Eng. J.* **268** 219-29.