Modeling and Simulation of Water-Gas Shift Reactors with and without Membrane

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Abstract: The objective of this study is to investigate the usage of membrane reactor technology in the water-gas shift reaction. Furthermore an assessment of the optimum parameters for the maximum conversion of carbon monoxide was carried out. The water-gas shift reaction is a well-known step for upgrading carbon monoxide to carbon dioxide in the production of purified Hydrogen gas. More recently, a renewed interest in the water-gas reaction carried out in hydrogen selective membrane reactors has been observed, because of the growing use of polymeric electrolyte membrane fuel cells, that operate using high-purity hydrogen. Membrane reactors are viewed as an interesting technology in order to overcome the equilibrium conversion limitations in non-membrane reactors. Firstly, the modelling and simulation of the reactor without membrane was carried out, and the obtained results were validated against the experimental published results, then the membrane reactor was simulated by employing a Hydrogen-selective Palladium membrane. A one dimensional steady state model was developed; mass and heat balances were solved simultaneously using MATLAB software. It was found that the conversion of carbon monoxide reaches a maximum of 29% for the non-membrane reactor and 90% for the membrane reactor, which represents an improvement of 210%. It was found that the optimum operating condition for membrane reactor were temperatures of 740 K, pressure of 10 atm and a reactor length of 115 cm.

Keywords: Membrane reactor, simulation, gas shift, Hydrogen, equilibrium conversion.

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1. INTRODUCTION

Water-Gas Shift Reaction (WGS R) equation below:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad (1)$$
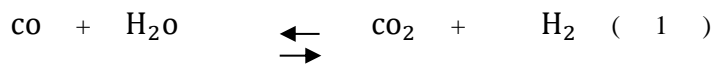
Is a reaction traditionally used for the production of Hydrogen from synthesis gas which is further used for ammonia production in the fertilizer industry, petroleum refineries for a variety of operations and recently as fuel for power generation and transportation. In this reaction water in the form of steam is mixed with carbon monoxide to obtain hydrogen and carbon dioxide. The use of gasification for power generation has also increased the use of water gas shift reactors multifold. The earliest recording of the reaction dated back to 1888 (Rhodes et al., 1995), and its prominence came with the Haber ammonia synthesis process and development of catalyst by Bosch and Wilde in 1912 (Twigg, 1989).

A catalytic membrane reactor (CMR) is a combination of a heterogeneous catalyst and a perm selective membrane, which is a thin film or layer that allows one component of a mixture to selectively permeate through it (Armor, 1989).

A CMR usually operates at higher yields, better reaction selectivity, and lower cost than a separate catalytic reactor and downstream separation units (Noble and Stern, 1995).By the early 1980s membrane technology had developed to the point at which a number of industrial groups began to consider using membranes to control the products of chemical reactions (Richard, 2004).Though the use of CMRs is not widespread. The development of new membranes, particularly porous ceramic and zeolite membranes, creates the potential to significantly improve yields of many catalytic processes (Noble and Stern, 1995).Recently, MRs are being developed for conventional

Chemical separations (Kemmere *et al*., 2001). Itoh (Itoh, 1990) stated, however, that for practical applications of membrane reactor technology, further developments of technology to manufacture membranes that possess high selectivity, high permeability, and high temperature durability are necessary .Roth (Roth, 1990), in a review of the future opportunities in industrial catalysis, indicated that we are at a threshold of major changes in separation technology (particularly in a shift from distillation to separation by synthetic membranes), and these changes will have substantial impact on chemical process technology. He further pointed out a number of opportunities for CMRs for equilibrium limited reactions, such as the production of ethylene from ethane, ammonia synthesis, methanol synthesis, and the water gas shift reaction.

The main goal of this study is to evaluate the Membrane Reactor (MR) ability to increase the yield of product and in order to assess the carbon monoxide conversion improvement through the use of this technology and also to investigate the effects of varying temperature, pressure and reactor length on the reactor performance.

2. PROBLEM STATEMENT

Water-Gas Shift Reaction is reversible and exothermic ($\Delta H= -41.2$ KJ/mol), therefore the equilibrium constant increases with decreasing temperature, but the reaction rate decreases with decreasing temperature(Bustamante *et al*., 2002) for this reason WGSR is thermodynamically unfavourable at elevated temperature (Smith *et al*., 2010), and equilibrium conversion limitations occurs in the non-membrane reactors (NMRs).

If one product preferentially permeates through the membrane, then this reaction that is limited by thermodynamic equilibrium

can obtain higher overall conversion (than could be obtained in NMRs), or operate at a lower temperature to obtain the same conversion. The equilibrium constant is not changed, but the product is removed from further contact with the catalyst so that it cannot react by the reverse reaction. This has been the approach used most often in CMR studies (Noble and Stern, 1995).

3. MATERIALS AND METHODS

In this section for both types of reactor mathematical modelling were developed and validated using Sing and Saraf (1980) experimental data. The simulation is divided into two sections. The first one is only concerning the reaction where the products remain in the reactor section. The reactor is traditional packed bed reactor (PBR), in which the maximum attainable reaction conversion is intrinsically limited by the equilibrium. Following the MR, which besides the chemical reaction is concerning the permeation of one product of the reaction through the wall (Hydrogen-selective membrane).

The isothermal simulations were done using MATLAB software.

3.1 Packed Bed Reactor

3.1.1 Rate Equation

The WGSR over a low-temperature catalyst, similar to that over a high-temperature catalyst, has been used. This rate equation takes into account the effects of temperature, pressure, and age of the catalyst on the catalyst activity. It also considers the reduction in reaction rate due to diffusion resistances. The following equation has been used to represent the rate of the shift reaction over the catalyst pellets (Singh and Saraf, 1980).

$$r = E_{ff} \times 2.955 \times 10^{13} \exp\left(\frac{-20960}{R \times T}\right) \times A_{gf} \times P_f \quad (\quad x_{co} - x_{co}{}^* \quad) \quad (2)$$

Where:

r is rate of reaction,($\frac{cm^3 \text{ of } H_2}{h.g \text{ of catyst}}$).

R is gas constant,($\frac{cal}{g.mol \, K}$).

T is temperature, K.

E_{ff} is the effectiveness factor which accounts for intrapellet diffusional resistance.

A_{gf} is an aging factor which accounts for loss in activity of the catalyst with usage.

Aging is the loss of catalytic activity due to a loss of active surface area resulting from the prolonged exposure to high gas-phase temperatures. This has been correlated with temperature and age from the data reported for the catalyst (Singh and Saraf, 1980) as:

$$\log A_{gf} = (4.66 \times 10^{-4} - 1.6 \times 10^{-6}T) \times \tau \quad (3)$$

Where:

τ is the age of the catalyst, (days).
P_f is accounts for the effect of pressure on the rate of reaction, the following expression valid for HT catalysts has been used here :

$$P_{f=} P^{(0.5-(P/250))} \quad (4)$$

P is total pressure, (atm).

Also:

x_{co} is mole fraction of CO.

$x_{co}{}^*$ is mole fraction of CO in equilibrium condition.

$$x_{co}{}^* = (x_{H_2} \times x_{co_2})/(x_{H_2o} \times k_{eq}) \quad (5)$$

Where:

x_{H_2} is Mole fraction of H_2 in equilibrium condition.

x_{co_2} is mole fraction of co_2 in equilibrium condition.

x_{H_2o} is mole fraction of H_2O in equilibrium condition.

k_{eq} is equilibrium constant.

$$k_{eq} = \exp[((\frac{9998.22}{T}) - 10.213 + 2.7465 \times 10^{-3}T - 0.453 \times 10^{-6}T^2 - 0.201 \times \ln T)/R] \quad (6)$$

3.1.2 Description of Mathematical Model:

A general mass balance can be written as follow:
Accumulation $_i$=In$_i$- Out $_i$ − Permation$_i$+ Genration$_i$ (7)

Where Accumulation$_i$ is the rate of accumulation of for species i , In$_i$ is the input flow rate, Out $_i$ is the output rate flow, Permation$_i$is the rate flow of permeation,Genration$_i$the rate of generation by chemical reaction.

In this study it was considered isothermal operation and the system in steady-state and then the term that refers to accumulation does not exist therefore, the general balance for a traditional packed-bed reactor becomes:

$$Out_i - In_i = Genration_i \quad (8)$$

Obviously, the permeation term only appears in the membrane reactor.

The high temperature shift reactors are single bed adiabatic reactors for which the following mathematical model has been developed. A differential cross section of the catalyst bed is considered throughout which temperature and composition are assumed constant. Axial diffusion of mass and heat has been neglected. The material and energy balance over such a differential section subject to the above assumptions yield the following equations which describe the composition and temperature of the reaction system along it (Singh and Saraf, 1980).

The system of differential equations:

$$\frac{dx_{co}}{dv} = -r \times \frac{w}{G} \quad (9)$$

$$\frac{dx_{H_2o}}{dv} = -r \times \frac{w}{G} \quad (10)$$

$$\frac{dx_{co_2}}{dv} = r \times \frac{w}{G} \quad (11)$$

$$\frac{dx_{H_2}}{dv} = r \times \frac{w}{G} \quad (12)$$

$$\frac{dx_{N_2}}{dv} = 0 \quad (13)$$

$$\frac{dT}{dv} = r \times \frac{-H}{\sum Cp} \times \frac{w}{G} \quad (14)$$

Where:

w is mass of catalyst (g) = Density of catalyst (g/cm^3) × volume of catalyst (cm^3)

−H is the Heat of reaction at T(cal/mol)= H0 + $\left(\left(Cp_{co_2} + Cp_{H_2}\right) - \left(Cp_{co} + Cp_{H_2o}\right)\right) \times (T - T_{reff})$

T_{reff} is Reference Temperature (K) = 298.15

v is dimensionless position along the reactor axial direction.

$$\sum Cp = x_{co} \times Cp_{co} + x_{H_2o} \times Cp_{H_2o} + x_{co_2} \times Cp_{co_2} + x_{H_2} \times Cp_{H_2} + x_{CH_4} \times Cp_{CH_4} + x_{N_2} \times Cp_{N_2} \quad (15)$$

3.1.3 Feed mole fractions

The initial values (Singh and Saraf, 1980):

$x_{co}= 0.011$, $x_{H_2o} = 0.448$

$x_{co_2}= 0.094$, $x_{H_2}= 0.343$

$x_{CH_4}= 0.001$, $x_{N_2}= 0.111$

3.1.4 Catalyst Specification

For both type of reactor the same catalyst specification is used as follow (Singh and Saraf, 1980):

Type: (Fe_2O_3-Cr_2O).

Volume: 3×10^4 (cm^3).

Density: 5.09 (g/cm^3).

3.1.5 Operating conditions

The same operating conditions for the both type of reactor are used as follow:

Temperature (T) = 675(k).

Pressure (P) = 3 (atm) at which the reacting gaseous system can be considered ideal.

Volumetric flow rate: (G) = 2533176×10^4(cm^3/h).

Gas constant (R) = 1.987 ($\frac{cal}{g.mol\,K}$).

Age of the catalyst (τ)= 98×24 (h).

Effectiveness factor (E_{ff}) = 1(Pseudo homogenous model).

3.2 Membrane Reactor

The same mathematical modelling equations , operating conditions , catalysts specification and feed mole fractions that used for Packed Bed Reactor are used for Membrane Reactor the only difference is in the hydrogen mass balance equation because only hydrogen permeates through the membrane, the mass balance for membrane reactor can written as:

$$Out_{H_2} - In_{H_2} = Genration_{H_2} - Permation_{H_2} \quad (16)$$

$$\frac{dx_{H_2}}{dv} = \frac{(r \times w)}{G} - \frac{A \times J_H \times (\frac{R \times T}{P})}{G} \quad (17)$$

J_H is thehydrogen flux through membrane ($\frac{mol}{cm^2.h}$) .

A is the membrane surface area (cm^2) .

$$A = \pi \times D \times L$$

Where D = 20 cm and L= 100 cm.

L/D= 5 (It is high ratio to improve the mass transfer between the reactants and the catalyst).

Pd or Pd-alloy membranes show very high hydrogen selectivities (Mendes *et al.*, 2009) therefore it has been used. The hydrogen flux through Pd and Pd-alloy membranes can be illustrated by the following equations:

$$J_H = \frac{P_e}{\delta} [(P_R)^n - (P_P)^n] \quad (18)$$

$$P_e = P_e^{\,\circ} \exp (\frac{-Ea}{R \times T}) \quad (19)$$

where $P_e$is the permeability, $0.5 < n < 1$, $P_e^{\,\circ}$ is the pre-exponential factor, Ea is the apparent activation energy, R is the ideal gasconstant, T is the absolute temperature, P_R and P_P are the hydrogen partial pressure on the retentate and permeate sides, respectively, and δ is the membrane thickness.

4. RESULTS AND DISCUSSION

4.1 Model validation

The result from the model equations of compositions and temperature in comparison with Singh and Saraf experimental result are represented in table 1

From Table 1 it can be seen that the difference in calculated and measured compositions and temperature at the reactor exit is insignificant. The agreement between the measured and calculated compositions and temperature at the outlet does indicate the validity of the model.

From Table 2 it can be seen that the membrane reactor achieves considerable improvement in conversion as compared with the traditional reactor in similar operating condition. It is worth noting that the maximum conversion that can theoretically be obtained in the traditional reactor, imposed by the equilibrium condition, can be overcome with the membrane reactor as a consequence of the hydrogen withdrawal from the reaction system according to Lechatlier´s principle. The conversion of carbon monoxide reaches a maximum of 42% for the PBR and 90% for the MR, which represents an improvement of 114%.

Table 1. Experimental data and calculate result for the PBR

	Packed Bed Reactor	Membrane Reactor
Temperature (K)	675	675
Pressure (atm)	3	3
Feed Flow Rate ($\frac{cm^3}{h}$)	2533176×10^4	2533176×10^4
Catalyst Type	$Fe_2O_3 - Cr_2O_3$	$Fe_2O_3 - Cr_2O_3$
Catalyst Weight (g)	9365×10^3	9365×10^3
Inlet CO Mole Fraction (x_{in})	0.011	0.011
Out let CO Mole Fraction (x_{out})	0.0064	0.0011
CO Conversion (X_{CO}) $X_{CO} = \frac{x_{in}-x_{out}}{x_{in}} \times 100\%$	42%	90%

Table 2. Comparison between the reactors with and Without membrane

Composition of the gas	Inlet % (dry basis)	Outlet % (dry basis) (experimental)	Outlet % (dry basis) (MATLAB)
CO	01.90	00.20	00.22
H_2	60.60	61.00	62.30
CO_2	17.10	18.60	18.80

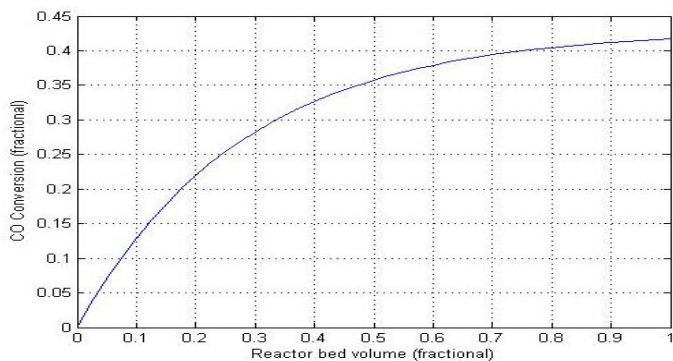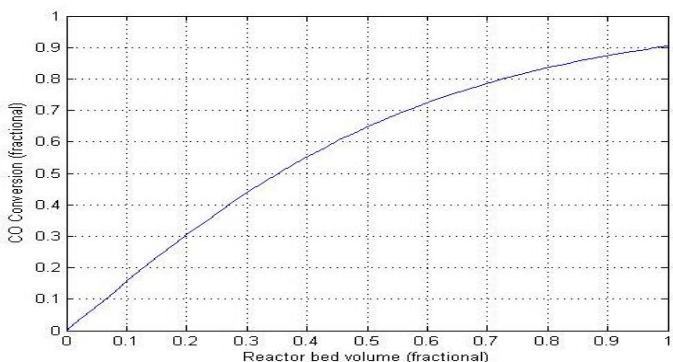|			
CH$_4$	00.20	00.20	00.20
N$_2$ + Ar	20.20	19.90	20.10

Fig.1. Packed Bed Reactor Profile

Fig.2. Membrane Reactor Profile

4.2 Sensitivity Analysis

For different ranges of operating conditions sensitivity analysis was developed for both types of the reactor.

4.2.1 Temperature Effect

In **Fig.3** the following data is used for the both reactor configurations:

Reactor length = 100 (cm), reactor diameter = 20 (cm), pressure = 3 (atm), feed flow rate = 2533176×10^4 ($\frac{cm^3}{h}$). The temperature is varied from 450 K to 750 K to find out the optimum temperature for the maximum CO conversion.

It can be seen that the CO conversion for Packed Bed reactor increases asymptotically with temperature. The conversion reaches a maximum conversion of 45% at a temperature of 600 k. Thus the temperature of 600 K is the optimum temperature for the Packed Bed reactor. At this temperature the conversion for Membrane reactor is 65%.

An increase in temperature beyond it optimum value for the Packed Bed reactor, result in a decrease in conversion due to the reversibility of the chemical reaction. Therefore equilibrium limitation is the limiting factor. The conversion approaches zero for Packed Bed reactor at temperature of 744.5 K. At this temperature the conversion for the Membrane reactor is 94.4%, which the maximum conversion for this reactor, thus the temperature of 744.5 K is the optimum temperature for the reactor operation.

4.2.2 Pressure Effect

In **Fig.4** the following data is used for the both reactor configurations:

Reactor length = 100 (cm), reactor diameter = 20 (cm), temperature = 675 (k), feed flow rate = 2533176×10^4 ($\frac{cm^3}{h}$) .The pressure is varied from 1 (atm) to 6 (atm) to find out the optimum pressure for the maximum CO conversion.

It can be seen that for the Packed Bed reactor the pressure has a positive effect in CO conversion up to equilibrium. At equilibrium the conversion reaches a maximum of 42% at a pressure of 3 atm. After this point no significant change occurs in the CO conversion with pressure. This is because the total number of moles of reactant in the gas phase at any axial position in a fixed bed reactor is not determined by the relative position of the forward and reverse reactions. At equilibrium the CO conversion is only function of temperature and feed composition.

For membrane reactor it can be seen that the CO conversion at a pressure of 3 atm increased to 90% from the 42% of the Packed Bed reactor. At a pressure of 6 atm the CO conversion reaches a maximum of 96% which is the optimum pressure for the reactor operation.

4.2.3 Reactor length effect

In **Fig.5** the following data is used for the both reactor configurations: Reactor diameter = 20 (cm), pressure = 3 (atm), feed flow rate = 2533176×10^4($\frac{cm^3}{h}$), temperature = 675 (k). The reactor length is varied from 20 (cm) to 140 (cm) to find out the optimum length for the maximum CO conversion.

It can be seen for the Packed Bed reactor the optimum length is 100 cm at which the CO conversion reaches the maximum of 42%. There is economically an unjustifiable increase in conversion beyond this point.

For the Membrane reactor length has positive effect in CO conversion. At the length of 140 cm, the CO conversion reaches 95% which the optimum length for reactor operation.
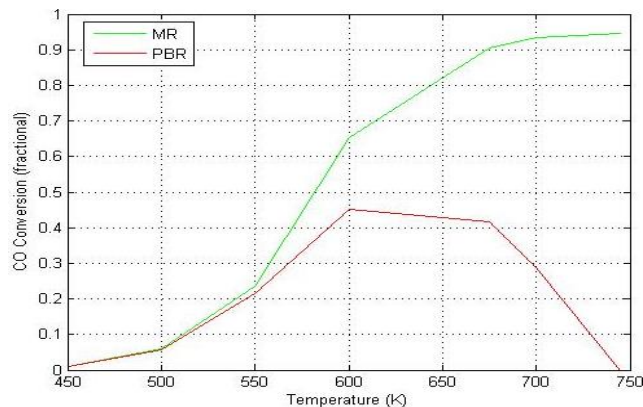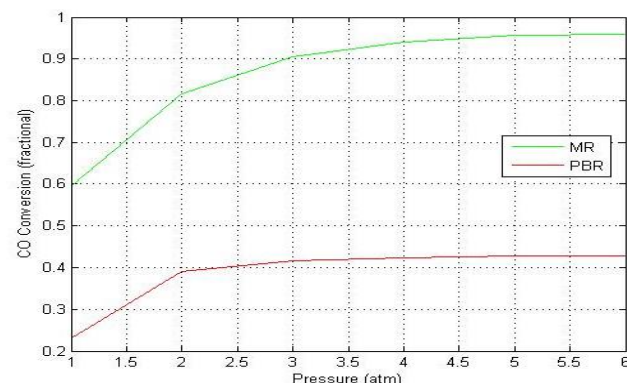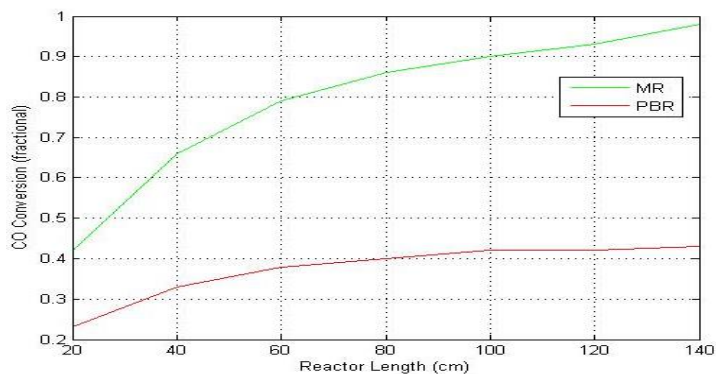

Fig.3. CO Conversion VS Temperature

Fig.4. Carbon monoxide conversion (fractional) VS Pressure

Fig.5. Carbon monoxide Conversion (fractional) VS Reactor Length

5. CONCULUSION AND RECOMENDATION

In conclusion the conversion of carbon monoxide reaches a maximum of 42% for the NMR and 90% for the MR, which represents an improvement of 114%. By developing sensitivity analysis for different ranges of operating conditions, it was found that the optimum operating conditions for membrane reactor were: temperature of 744.5 (k), pressure of 6 (atm) and a reactor length and diameter of 140 (cm), and 20 (cm), respectively. The study recommends a model validation should be carried out experimentally to confirm the reported findings and complete economic analysis should be carried out to assess the commercial viability of the usage of membrane reactor for the gaseous reversible reactions.

NOMENCLATURE

A   Membrane surface area (cm^2)

A_{gf} Aging factor which accounts for loss in activity of the catalyst with usage

Cp_i Heat capacity of component i

D   Reactor diameter (cm)

Ea   Apparent activation energy

E_{ff} Effectiveness factor

G   Volumetric flow rate(cm^3/h)

H   Heat of reaction at T(cal/mol)

J_H The hydrogen flux through membrane ($\frac{mol}{cm^2.h}$)

k_{eq} Equilibrium constant

L   Reactor length (cm)

P   Total pressure

P_P Hydrogen partial pressure on the permeate sides

P_f accounts for the effect of pressure on the rate of reaction

P_e Permeability

P_R Hydrogen partial pressure on the retentate and

R   Gas constant,($\frac{cal}{g.molK}$)

r   Rate of reaction,($\frac{cm^3 of\ H_2}{h.g\ of\ catyst}$)

T   Temperature, (K)

T_{ref} Reference Temperature (K)

w   Mass of catalyst (g)

x_i Mole fraction of component i

x_{co}^* Carbon monoxide mole fraction at equilibrium condition.

Greek letters

δ Membrane thickness

τ Age of the catalyst (h)

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