막반응기를 이용한 수성가스 전환반응의 모사

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Simulation Study for Water-Gas Shift Membrane Reactor

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1. Introduction

In recent years, there has been a renewed interest in the water-gas shift (WGS) reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$\Delta H = -41.2 \text{ kJ/mol}, \Delta G = -28.6 \text{kJ/mol}$$

because of its potential use in conjunction with fuel-cell power generation[1].

A membrane reactor concept, which combines the typical characteristics of chemical reaction with separation process, has been analyzed and simulated in this study. The advantages of the use of a membrane reactor include chemical equilibrium shift towards higher reactant conversion and purer product than the traditional reactors.

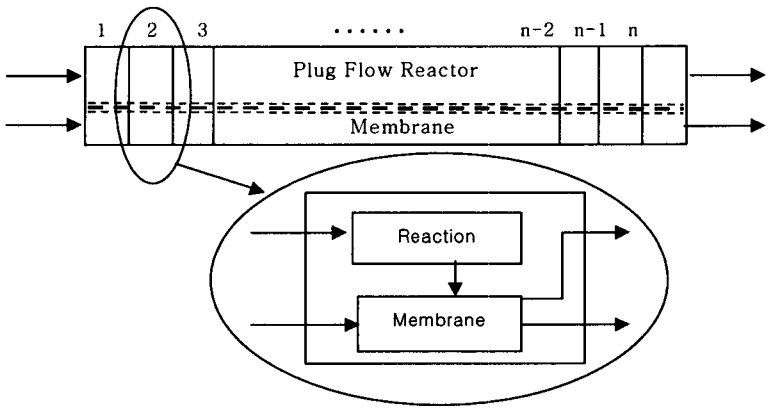

Fig 1. The proposed membrane reactor model

2. Experiment

A membrane reactor model that incorporates a catalytic reaction zone and a separation membrane is proposed. The water-gas shift reaction to produce hydrogen was chosen as a model reaction to be investigated. The overall concept of the proposed model is depicted

below. The membrane reactor is divided into smaller parts by number of n, and each part (named CELL) that contains both reaction and product separation function is modeled. One of the membrane outlet streams is connected to the next cell, which is repeated up to the last cell.

From previous theoretical results[2], it appeared that the kinetic for membrane reactors can be different from the kinetic studied in a traditional reactor because of the changes of the type of contact between catalyst and reactants, contact time and of the concentration of species[3]. For that reason, in the simulation program both kinetic expressions used in the previous work continue to be considered.

Langmuir-Hinshelwood's kinetic expression[4]:

$$r = k\frac{K_{CO}K_{H_2O}\left(P_{CO}P_{H_2O} - \frac{P_{CO_2}P_{H_2}}{K_{eq}}\right)}{(1 + K_{CO}P_{CO} + K_{H_2O}P_{H_2O} + K_{CO_2}P_{CO_2})^2}\rho_{cat}/60 \text{ (mol/g\_cat min)}$$

Temkin's kinetic expression[5]:

$$r = k\frac{\left(P_{H_2O}P_{H_2O} - \frac{P_{H_2}P_{CO_2}}{K_{eq}}\right)}{AP_{H_2O} + P_{CO_2}} \text{ (s}^{-1}\text{)}$$

Equilibrium constant K_{eq} :

$K_{eq} = \exp(4577.8 / T \ 4.33)$

The permeability of Hydrogen through the palladium is [2]

$Pe = 2.95 \ 10\text{-}4 \exp(-5833.5 / T)$

Kinetic parameters for water-gas shift reaction and membrane-related data are adopted from the literature. The plug flow reactor with Pd membrane (0.070 ~ 0.075 mm thick) investigated is 150mm long, 8mm inner diameter, 9.64g of Cu/ZnO/Al2O3 catalyst packed. Operation conditions are shown table 1.

table 1. Mole fraction of streams

material	CO	H2O	CO2	H2	N2
Feed	0.237	0.260	0.089	0.030	0.384
Sweep Gas	0.000	0.000	0.000	0.000	1.000

3. Results

According to Fig. 2, proposed model works well for membrane reactor at middle time factors. In higher time factor (low flow rate) area, experimental data shows that CO conversion is 95% above[2], simulation result reach at 86% above.

As expected, two results of simulated and experimental are shown that equilibrium value can be overcome by using Pd membrane reactor.

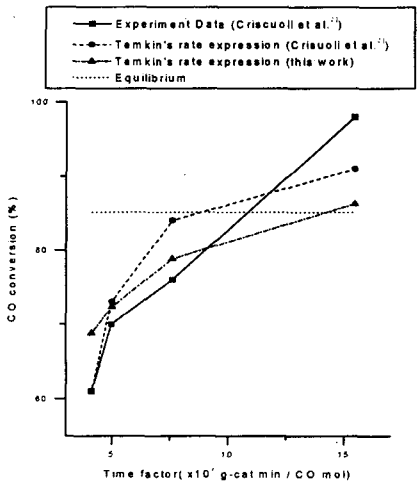

Fig. 2. A comparison between simulation ressult and literature data
(T = 595K, P_{feed} = P_{sweep} = 1atm(g), Q_{sweep} = 0.1168mol/h, Q_{feed} = 0.1582mol/h)

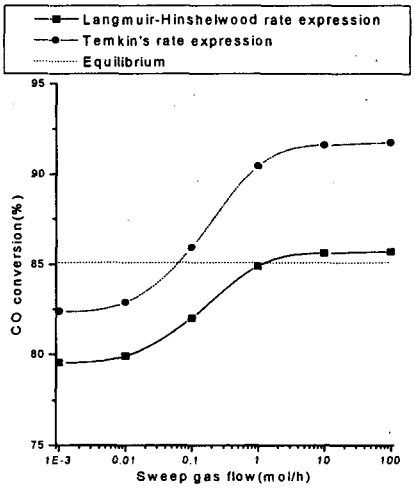

Fig. 3. Effect of sweep gas flow rate on the CO conversion for Pd membrane reactor model (T=595K, P_{sweep} = P_{feed} = 1atm(g), Q_{feed} = 0.1582mol/h)

Simulation result for an effect of sweep gas flow rate on Pd membrane reactor was plotted for figure 3. For this case, best sweep gas flow rate is 0.8~1.0 mol/h and molar fraction of hydrogen is 0.03~0.05.

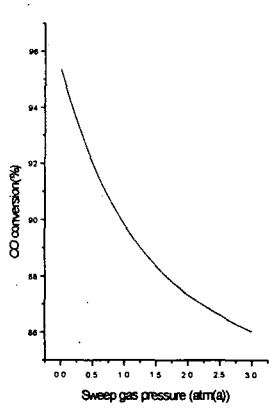

Fig 4. Effect of sweep gas pressure (T=610K, P_{feed}= 2atm(a), Q_{feed}=0.1582mol/h, Q_{sweep}=0.1168mol/h)

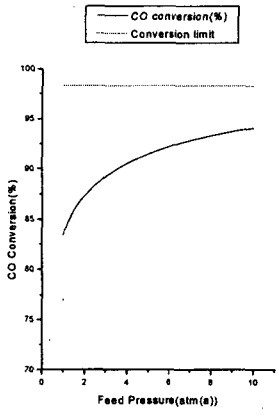

Fig 5. Effect of reactant feed pressure (T=610K, Q_{feed} = 0.1582mol/h, Q_{sweep} = 0.1168mol/h, P_{sweep} = 2atm(a))

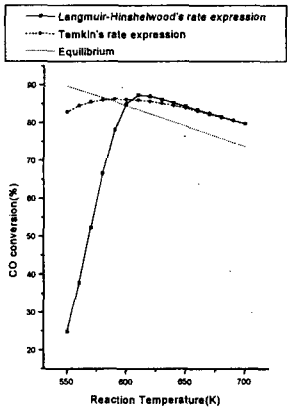

Fig 6. Effect of reactant temperature on the CO conversion (P=1atm(g), Q_{feed}=0.1582mol/h, Q_{sweep} = 0.1168mol/h)

Figure 4~5 show effects of sweep gas pressure and reactant feed pressure on CO conversion. Because permeability of hydrogen depends on lumen and shell side hydrogen partial pressure, CO conversion grows down to increase the sweep gas pressure, and to decrease reactant feed pressure.

Reaction temperature effect on the CO conversion was plotted against figure 6. Maximum point of CO conversion was appeared at 580~610K.

4. Conclusions

New method for modeling and simulation of a membrane reactor is developed in this work, which is tested by being applied to water-gas shift membrane reactor.

The simulation result shows good agreement with experimental data, whichcan be used for various purposes including decision of optimum operating condition and membrane reactor design.

The simulation result suggest that optimum operating conditions of water-gas shift membrane reactor are:

1. Temperature : 580~610K
2. Feed pressure : higher than sweep gas pressure (around 3~4 atm)
3. Sweep gas rate/H_2O rate = above 15

5. Acknowledgement

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