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분리막 반응기를 이용한 천연가스 개질반응의 성능에 관한 비교 분석

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Comparative studies for the performance of a natural gas steam reforming in a membrane reactor

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요 약

본 연구에서는 다양한 수소 생산 방법 중 하나인 천연가스 수증기 개질반응(natural gas steam reforming reaction)에 대해 일반적인 충전층반응기와 반응기와 수소분리기가 결합된 새로운 형태의 분리막 반응기에서의 성능에 대한 비교분석을 수행하였다. Xu 와 Froment에 의해 기존에 발표된 실험결과를 바탕으로 상업용 화학공정모사기인 Aspen HYSYS® 모델이 개발되었으며, 반응온도, H_2 투과량, Ar 유량 등이 분리막 반응기에서의 반응물의 전환율 및 H_2 수율 향상도에 미치는 영향에 대해 분석한 결과 분리막 반응기에서 보다 많은 양의 수소 수율 및 메탄전환율이 확인되었다. 더 나아가, 전체 시스템에서 필요로 하는 열량을 공급하기 위해 요구되는 천연가스의 양에 초점을 맞춰 분리막 반응기에서의 원가절감 가능성을 평가한 결과, 분리막 반응기에서 10.94%의 원가절감이 관찰되었다.

Abstract - For a natural gas steam reforming, comparative studies of the performance in a conventional packed-bed reactor and a membrane reactor, a new conceptual reactor consisting of a reactor with series of hydrogen separation membranes, have been performed. Based on experimental kinetics reported by Xu and Froment, a process simulation model was developed with Aspen HYSYS®, a commercial process simulator, and effects of various operating conditions like temperature, H_2 permeance, and Ar sweep gas flow rate on the performance in a membrane reactor were investigated in terms of reactant conversion and H_2 yield enhancement showing improved H_2 yield and methane conversion in a membrane reactor. In addition, a preliminary cost estimation focusing on natural gas consumption to supply heat required for the system was carried out and feasibility of possible cost savings in a membrane reactor was assessed with a cost saving of 10.94% in a membrane reactor.

Key words : natural gas steam reforming, hydrogen, membrane reactor, cost estimation

I. Introduction

Due to the high demand for hydrogen in various fields such as ammonia production, chemical industry/refineries, electronic industry, metal/glass industry, and food industry as shown in Fig. 1 [1], much attention has been paid to a variety of methods for effective hydrogen production and diverse methods like methane steam reforming (MSR) [2,3], methane dry reforming (MDR) [4,5], methanol steam reforming [6,7], ethanol steam reform-

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ing [8,9], partial oxidation, water-gas shift reaction (WGSR), water electrolysis, biomass gasification, pyrolysis, and plasma reforming [10-13] have been used for hydrogen production. In particular, a MSR using natural gas as fuel converts methane to carbon monoxide and hydrogen, a synthesis gas (syngas), as shown in Equation (1) and accounts for about 48% of global hydrogen production [14].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

A MSR in a conventional packed-bed reactor (PBR) requires high reaction temperature ranging from 973 to 1373K and needs an additional hydrogen purification unit like pressure swing adsorption (PSA) [15,16]. To compensate the drawbacks, a membrane reactor (MR) combining a reactor and a separator has been proposed as a means to produce more H_2 and to reduce an operating temperature simultaneously due to equilibrium shift by *Le Chatelier*'s principle [17,18].

In this paper, comparative studies for effects of temperature, H_2 permeance, and Ar sweep gas flow rate on the reactant conversion enhancement and hydrogen yield enhancement in a MR compared with a PBR are performed to assess the benefits of using a MR. In addition, a preliminary cost estimation focusing on an annual operating cost in terms of natural gas usage to supply heat required for the system is carried out based on simulation

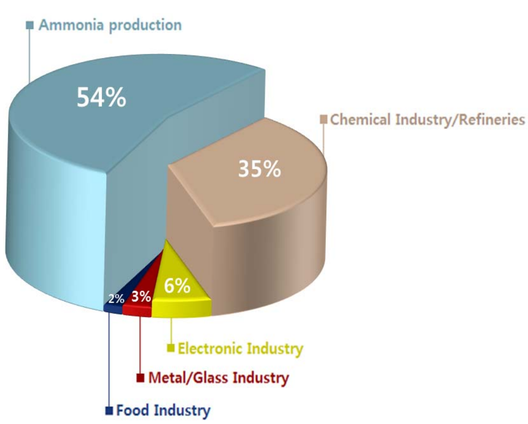

Fig. 1. A diagram for distribution of a global hydrogen market.

results obtained from Aspen HYSYS®, a commercial chemical process simulator.

Ⅱ. Methods

To simulate proposed processes of interest, commercial process simulators such as Aspen HYSYS® (AspenTech, USA) [19-21], Aspen Plus® (AspenTech, USA) [22-24], Unisim Design® Suite (Honeywell, USA) [25-27], and CHEMCAD (Chemstations, USA) [28-30] are widely used to obtain the useful information and an optimized process model based on material and energy balance. Among them, Aspen HYSYS® was used in this study to simulate the process with most well-known MSR kinetics reported by Xu and Froment [2] and the Peng-Robinson fluid package as a suitable equation of state assuming a steady state.

2.1. A packed-bed reactor (PBR)

Fig. 2 presents a process flow diagram (PFD) of a natural gas steam reforming (NSR) using Aspen HYSYS® for a conventional PBR equipped with a boiler to provide enough heat required in the system. As shown in Fig. 2., multiple compressors were used to pressurize natural gas from 1 to 27 bar, a pump was employed for water, and a reaction temperature ranging from 873 to 1023K was used for the simulation works. The composition of methane in natural gas was assumed to be 88.1% in this study [31]. In addition, natural gas usage for required heat in the proposed process was calculated and preliminary cost estimation was carried out based on the simulation results. The price of electricity required to operate three compressors and a pump was calculated based on an electricity price of \$0.07 kWh^{-1} in 2012 and was converted to a price in 2015 based on chemical engineering plant cost index (CEPCI) of 547.2 in 2015 [32,33].

2.2. A membrane reactor (MR)

Fig. 3 shows a PFD of NSR in a MR using Aspen HYSYS®. Since a membrane unit is not in the model library of Aspen HYSYS®, a membrane template consisting of a series of reactors and separators was created to reflect the functionality of a MR [34,35]. All reaction conditions and geome-

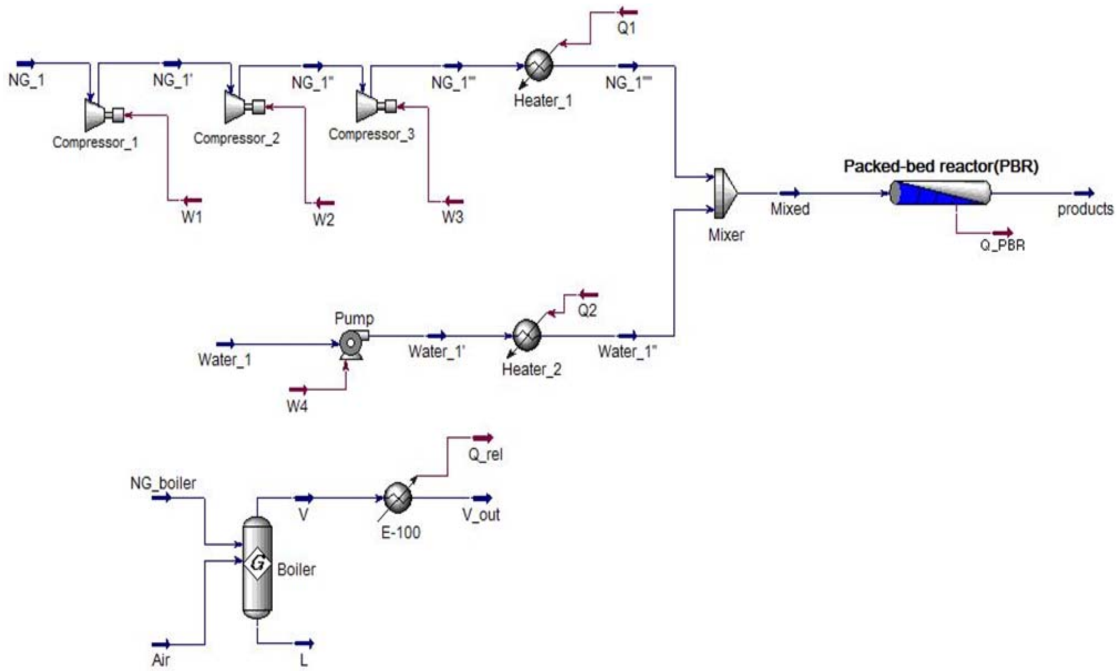

Fig. 2. Process flow diagram (PFD) of a system with a packed-bed reactor (PBR).

try are the same for both PBR and MR except that a MR have a hydrogen separation membrane inside the reactor.

III. Results and Discussion

3.1. Effects of H_2 permeance and Ar sweep gas in a MR

Fig. 4 demonstrates the effect of H_2 permeance (1×10^{-6}~1×10^{-5} mol m^{-2} s^{-1} Pa^{-1}) on H_2 enhancement, defined as H_2 yield increase in a MR compared with a PBR, with an Ar sweep gas as a driving force in a MR ranging from 1 to 100 kmol h^{-1} at 973K. For all H_2 permeance and Ar sweep gas flow studied, better performance in a MR was observed compared with a conventional PBR confirming a benefit of using a MR. Cleary, it was shown that H_2 permeance and Ar sweep gas flow rate was favorable for H_2 yield enhancement. However, little effect was observed for an Ar sweep gas flow rate of over 50 kmol h^{-1} providing a useful design guideline for the MR system.

3.2. Effects of H_2 permeance and operating temperature in a MR

With a selected Ar flow rate of 50 kmol h^{-1} obtained from simulation results, the effects of H_2 permeance and operating temperature on CH_4 conversion (X_{CH4}) enhancement were examined at 873-1023K. As shown in Fig. 5, X_{CH4} enhancement increased as permeance increased while it decreased as operating temperature increased and it is believed that higher methane conversions at higher temperatures due to an endothermic reaction of a NSR result in relatively small enhancements in a MR compared with a PBR. Again, better performance in a MR was observed for a wide range of H_2 permeance and operating temperature.

3.3. Preliminary cost estimation: operating cost

Economic analysis focusing on operating cost based on natural gas usage required for a boiler has been performed. From the results obtained from the process simulation works, a preliminary cost estimation was carried out for a conventional PBR and a MR with a fixed Ar sweep gas flow

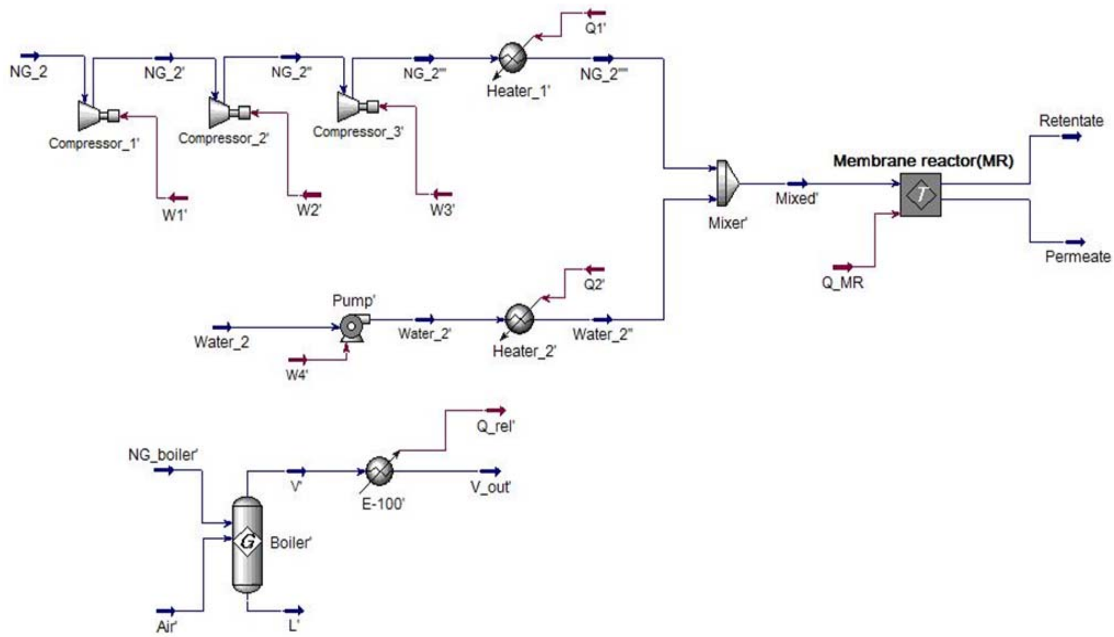

Fig. 3. Process flow diagram (PFD) of a system with a membrane reactor (MR).

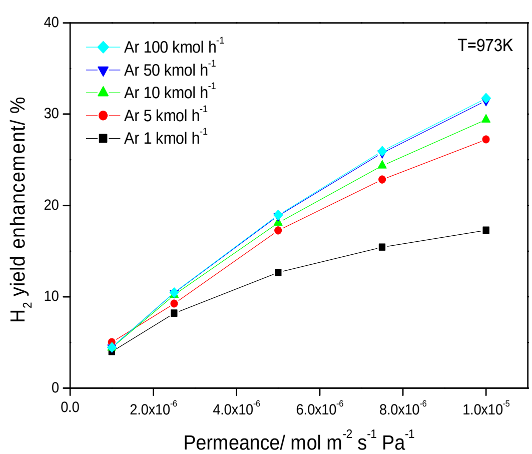

Fig. 4. Effect of permeance on H_2 yield enhancement with different Ar flow rates at 973K.

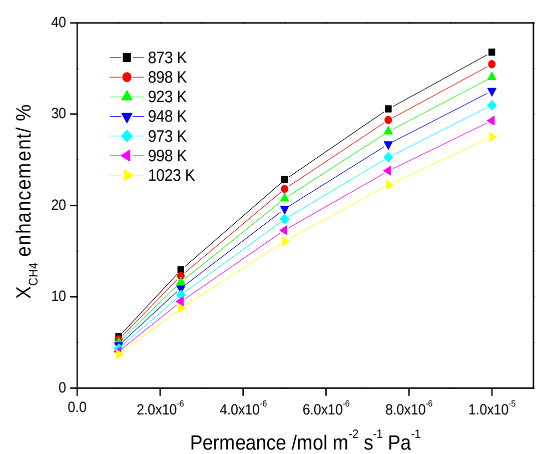

Fig. 5. Effect of permeance on methane conversion (X_{CH4}) enhancement at 873-1023K with a fixed Ar flow rate of 50 kmol h^{-1}.

rate of 50 kmol h^{-1} and H_2 permeance of 1×10^{-5} mol m^{-2} s^{-1} Pa^{-1}. It was found that the same amount of H_2 was obtained at a reaction temperature of 1023K and 936.9K in a PBR and a MR, respectively as shown in Table 1. With higher heating value (HHV) of methane (55.6 MJ kg^{-1}) and the current price of natural gas in Korea (₩11.16 MJ^{-1} from Korea Gas Corporation (KOGAS)), annual costs for natural gas usage and possible cost savings in a MR compared with a PBR were calcula-

Table 1. Preliminary cost estimation based on natural gas (NG) consumption

		Packed-bed reactor (1023K)	Membrane reactor (936.9K)
H_2 produced /kmol h^{-1}		0.982	
NG in a boiler /kmol h^{-1}		0.2084	0.1856
NG cost	/ MJ h^{-1}	186	166
	/ ₩ yr^{-1}	18,173,282	16,185,034
cost savings/ %		10.94	

ted. From the analysis, a cost saving of 10.94 % was observed in a MR showing the additional benefit of using a MR over a conventional PBR.

Ⅳ. Conclusions

Process simulation and preliminary economic analysis for a natural gas steam reforming (NSR) have been carried out for comparative studies in a packed-bed reactor (PBR) and a membrane reactor (MR) using a commercial process simulator, Aspen HYSYS®, with the previously reported kinetics by Xu and Froment. For all studied conditions, better performance was found in a MR compared with a PBR in terms of H_2 yield and CH_4 conversion enhancement due to equilibrium shift by *Le chatelier*'s principle. Further studies showed that H_2 permeance was favorable for enhancements in a MR while operating temperature was not. In addition, no further favorable effect of higher Ar sweep gas flow rate than 50 kmol h^{-1} was found in a MR and a preliminary cost estimation showed a cost saving of 10.94% in a MR confirming benefits of employing a MR for NSR.

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