International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 0229

INTEGRATED NATURAL GAS HYDRATE EXPLOITATION BY CH_4-CO_2/H_2 REPLACEMENT WITH METHANE REFORMING: CONCEPTUAL PROCESS DESIGN AND EXERGY ANALYSIS

Mengying Wang†1, Hongnan Chen†1, Chun Deng†1*, Xiaohui Wang1, Bei Liu1, Changyu Sun1, Guangjin Chen1*, Mahmoud El-Halwagi2

1 State Key Laboratory of Heavy Oil Processing, China University of Petroleum-Beijing, 18 Fuxue Road, Changping, Beijing, 102249, China

2 Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843, United States

ABSTRACT

The conventional methods for methane gas recovery from hydrate sediments require high investment but with low gas production efficiency and may cause potential environment and security problems. But the novel natural gas hydrate exploitation method by CO_2/H_2 replacement coupling methane reforming can improve the replacement effect and reduce the cost of gas separation. However, energy consumption and energy performance have not been investigated thoroughly. This work develops a detailed process simulation model and conducts an exergy analysis for producing hydrogen from the integrated natural hydrate gas exploitation with methane reforming via two different boundaries. Results show that the exergy ratio of the integrated process is 2.06, exergy efficiency of the hydrogen production process is 72.40 %, but exergy efficiency of the integrated process is much lower, which is 26.59 %.

Keywords: natural hydrate gas production, hydrogen production, methane reforming, exergy analysis, carbon dioxide sequestration

NONMENCLATURE

E_{H_2}	Total exergy of H_2, kW
$E_{H_2,physical}$	Physical exergy of H_2, kW
E_{MP}	Exergy of MP steam, kW
E_{dest}	Destroyed exergy, kW
$E_{un-used}$	Un-used exergy, kW
η_{ratio}	Exergy ratio
$\eta_{integrated}$	Exergy efficiency of integrated process
$\eta_{hydrogen}$	Exergy efficiency of hydrogen production process

1. INTRODUCTION

Natural gas hydrates (NGHs) are ice-like, non-stoichiometric crystalline solids consisting of water and natural gas under low temperature and high pressure. The global amount of technically recoverable natural gas from hydrates is in the order of 3×10^{13} m^3[1]. Developing and utilizing natural gas hydrates can help to meet the increasing energy demand, but also mitigate environmental impacts compared with fossil fuels.

The challenges of natural gas hydrate exploitation that need to be overcome at present is to reduce the investment, improve energy efficiency, avoid environmental and security problems as well[2]. The conventional methods for NGHs exploitation include depressurization, thermal stimulation, inhibitor injection and combined methods. To solve the problems of regular methods, the CO_2 replacement method is now considered a techno-economic feasibility hydrate production technology[1], as this promising technology cannot only enhance the recovery efficiency but also can sequestrate CO_2.

Rice[3] proposed a new hydrogen production mode from gas hydrates by steam reforming without the release of CO_2 to the atmosphere. Wang et al.[4] and Sun et al.[5] conducted an experimental simulation of gas production from hydrates by CO_2/H_2 replacement, and found the influence of composition of CO_2/H_2 and injection rate on methane production and CO_2 sequestration. At present, researchers are mainly focusing on demonstrating the technical feasibility of hydrate exploitation from experimental and numerical simulation, but have done less on its economic feasibility and energy efficiency. To improve energy efficiency in production process remains one of the key issues concerning the commercial exploitation of natural gas hydrate. Feng et al.[6] investigated the production performance of gas hydrate accumulation and energy ratio (the ratio of energy output to input) was used to evaluate the production process. However, the energy ratio based on the first law of thermodynamics, cannot comprehensively evaluate the whole production process and does not provide information about the location and cause of thermodynamic losses. Exergy analysis is a significant tool that can overcome the shortcomings of the energy analysis, yielding meaningful efficiencies for processes and systems to be effectively compared and evaluated. In this work, we conducted a conceptual process design of the novel natural gas hydrate exploitation method by CO_2/H_2 replacement coupling methane reforming and applied exergy analysis to two processes with different boundaries: the integrated natural gas hydrate exploitation process and hydrogen production process, pointing out the exergy flows, losses, and efficiency.

2. PROCESS MODELING

2.1 Process description

Fig 1 shows the process design of the integrated natural gas hydrate exploitation by CH_4-CO_2/H_2 replacement with methane reforming. The novel natural gas hydrate exploitation scheme is about using the produced methane by CO_2/H_2 replacement from the hydrate reservoir to generate hydrogen via methane reforming, CO_2/H_2 gas mixtures can be separated through membrane separation because part of CO_2/H_2 could be recycled to hydrate production process. Finally, a model of the whole process (injection, production, conversion and separation) of the natural gas hydrate exploitation system is developed. This novel model can take the advantages of gas mixture replacement for hydrate exploitation and hydrogen production, and reduce the cost of mixture gas separation process, as the separation process of mixture gas by CO_2/H_2 replacement is easier than that by CO_2/N_2 replacement.

The whole process is mainly divided into three parts: natural gas hydrate exploitation process, reforming and water gas shift process, and membrane separation process. Since the feed gas contains CH_4 and CO_2, the methane reforming process is characterized by the following main reactions:

$$CH_4 + CO_2 \longleftrightarrow 2CO + 2H_2 \quad \Delta H=247.3 \text{ kJ/mol} \tag{1}$$

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \quad \Delta H=206.3 \text{ kJ/mol} \tag{2}$$

Because of the endothermic reactions, heat must be provided to the reformer. In this process, the heat comes from combustion of fuel (heavy diesel), which can be shown in Fig 1. Waste heat from the combustor can be recovered to generate steam for reforming process and MP steam. After reforming, a water-gas shift reactor is used to convert CO further into CO_2 and H_2 using the available H_2O in the gas. The shift reaction is shown in Eq. (3). The final part of the process is gas separation. Hydrogen membrane separation technique is used in this work.

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \Delta H=-41.09 \text{ kJ/mol} \tag{3}$$

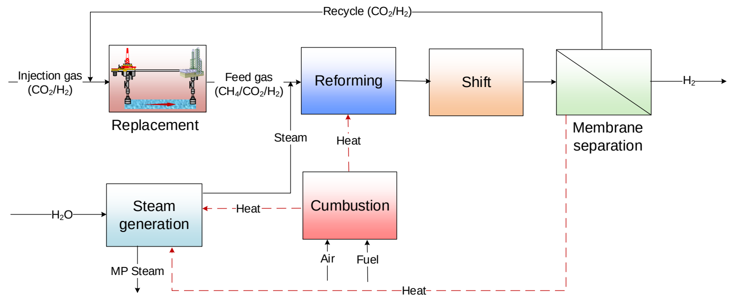

Fig 1 Conceptual diagram of the integrated natural gas hydrate exploitation with methane reforming

2.2 Simulation model

The integrated system model was developed via the computer-aided software Aspen HYSYS, and the process flow diagram is shown in Fig 2a. The CO_2/H_2 mixed gas sweep-replacement method is used in the natural gas hydrate exploitation process, and the production data used in the replacement production simulation process can be obtained from experiments. The composition and flow rate of injection gas and produced gas are shown in Table 1.

In Aspen HYSYS, REquil (chemical equilibrium reactor) was selected to simulate the two reactors and Flash 2 (two-phase flash evaporator) was selected to simulate the gas-liquid separator. In the membrane separation process, the hydrogen separation membrane is modeled using a Component Splitter and a Spreadsheet module. In order to produce high end stream H_2 purity (>99%) and meet the component demand of recycled gas, a three-stage membrane separation process is adopted using H_2 selective metalic membranes[7]. H_2 is on the permeate side and recycled CO_2/H_2 gas mixture is in the retentate. Since the natural gas hydrate exploitation process is set to inject gas at 8 MPa, the energy consumption of the subsequent pressurization process can be reduced by using recycled CO_2/H_2 gas mixture in the retentate. For heat integration, the pumped water is heated to steam by the stream from Shift reactor in HE1, waste heat from the combustor in HE3 and HE4, and stream from membrane separation in MemHE1 and MemHE2. The high temperature vapor from Shift reactor and Reformer is used to preheat the mixed gas in PreHE3 and PreHE4.

Table 1 Composition and flow rate of feed gas injection and produced gas[4,5]

	CH_4 (%)	CO_2 (%)	H_2 (%)	Flow rate (kmol/h)
Injection gas	0	72	28	190
Produced gas	48	27	25	177.2

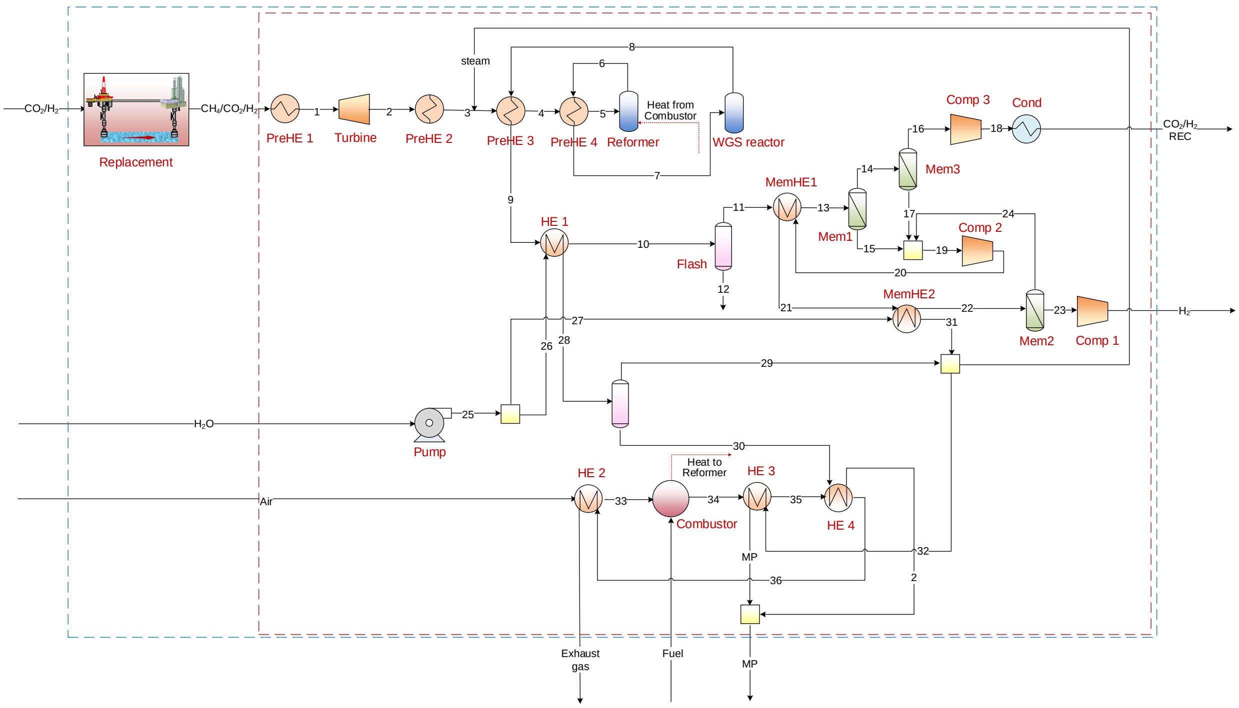

Fig 2 Process flowsheets. Dashed line represents the system boundary of (a) the integrated exploitation process (blue) and (b) hydrogen production process (red).

Table 2 Operating parameters for the process simulation

Component	Item	Value
Inlet fuel	T (°C)	25
	P (MPa)	0.1
Inlet water (BFW)	T (°C)	105
	P (MPa)	0.46
Inlet air	T (°C)	25
	P (MPa)	0.1
	O_2 (mol%)	20.34
	N_2 (mol%)	76.52
	H_2O (mol%)	3.103
	CO_2 (mol%)	0.0370
Injection gas	T (°C)	2.4
	P (MPa)	8
Reformer	T (°C)	890
	P (MPa)	3
	Minimum temperature difference (°C)	20[9]
Shift reactor	T (°C)	360
	P (MPa)	3
Pump	Efficiency (%)	80
Compressor	Efficiency (%)	80
Combustor	Efficiency (%)	91
Membrane	H_2/CO_2 selectivity	50[7]
	T (°C)	200[7]
	$P_{Permeate}$ (MPa)	0.15
	$P_{Retentate}$ (MPa)	2.3
	H_2 Purity (%)	>99
Heat exchangers	ΔT_{min} (°C)	10

Natural gas production from hydrates coupling methane reforming process involves polar substances, the SRK property method is used[8]. The detailed operating parameters are listed in Table 2. The model is validated and the simulation results are in good agreement of those reported by Su et al.[8].

3. EXERGY ANALYSIS

The energy performance of natural gas hydrate exploitation is commonly assessed by Energy Return on Investment (EROI)[10]. It means the ratio of output to input, and is based on the first law of thermodynamics, which is defined as:

$$EROI=\frac{output\ energy}{input\ energy} \quad (4)$$

However, the energy performance of gas hydrate exploitation can only be roughly measured using this indicator. In chemical processes, exergy analysis is normally conducted for improving system performance. Exergy analysis focuses on exergy flows, losses and efficiency of a system. And exergy efficiency can show the available energy performance, which is more sensible to evaluate the production process. In this work, exergy analysis is investigated within two boundaries: the integrated gas hydrate exploitation process with hydrogen production and hydrogen production process without exploitation. The boundaries are shown in Fig 2. The standard state for exergy analysis in this work is 25 °C and 1 atm. The exergy loss of the system is the difference between the exergy into and out of the system. It measures the unrecoverable exergy of the available energy into the system. The integrated process involves natural gas hydrate exploitation, not like a normal chemical process, the exergy out of the system (considering H_2 chemical exergy) is higher than the exergy into the system. Therefore, Exergy ratio is defined to evaluate the process. Different from EROI, it is based on the second law of thermodynamics. Exergy ratio and exergy efficiency of the system are both defined as the ratio of exergy recovered in hydrogen and MP steam to the total exergy into the system, which is given in Eqs. (5) and (6). To calculate the exergy efficiency of the integrated process, H_2 chemical exergy will not be considered, only considering physical exergy, which is defined in Eq. (7).

Table 3 lists the total exergy flows of the two processes: (a) integrated process and (b) hydrogen production process. The efficiencies of these two processes are shown in Table 4. Exergy ratio of the integrated production process is 2.06, indicating that the proposed natural gas hydrate exploitation scheme is meaningful. Due to the unconventional chemical process of gas hydrate production, the exergy efficiency of the integrated process is 26.59 %, lower than that of the hydrogen production process (72.40 %). The dominant exergy input, destroyed exergy and un-used exergy of the two processes are different. The destroyed exergy of the integrated process is much higher than that of the hydrogen production process, resulting in much lower exergy efficiency. Decreasing the fuel exergy input of the integrated process and recovering process waste heat properly can improve the exergy ratio and exergy efficiency.

Table 3 Exergy flows of the integrated and unintegrated processes

	Exergy (kW)	
Exergy in	a	b
E_{fuel}	5699.70	5699.70
E_{CH_4}	-	20168.17
E_{water}	309.58	309.58
W_{net}	4306.12	3628.82
Total	10315.40	29806.27
Exergy out		
E_{H_2}	19594.97	19594.97
E_{MP}	1984.20	1984.20
$E_{exhaust}$	408.28	2809.13
E_{dest}	7164.58	5417.97
$E_{un-used}$	7572.86	8227.10
Total	2071.94[1] 21987.45[2]	24388.30

[1] total output exergy without H_2 chemical exergy; [2] total output exergy with H_2 chemical exergy.

$$\eta_{ratio}=\frac{E_{H_2}+E_{MP}}{E_{in}} \quad (5)$$

$$\eta_{hydrogen}=\frac{E_{H_2}+E_{MP}}{E_{in}} \quad (6)$$

$$\eta_{integrated}=\frac{E_{H_2,physical}+E_{MP}}{E_{in}} \quad (7)$$

Table 4 Exergy efficiencies of the processes

Efficiencies	
η_{ratio}	2.06
$\eta_{integrated}$	26.59 %
$\eta_{hydrogen}$	72.40 %

4. CONCLUSIONS

The work performed a conceptual process design of the novel natural gas hydrate exploitation method by CO_2/H_2 replacement coupling methane reforming and developed the novel process model via Aspen HYSYS, which can bring a new sight to natural gas hydrate production. The exergy analysis of two processes with different boundaries: the integrated natural gas hydrate exploitation process and hydrogen production process without exploitation is conducted. The exergy analysis results showed that the exergy ratio of the integrated process is 2.06, exergy efficiency of the hydrogen production process is 72.40 %, but exergy efficiency of the integrated process is much lower, only 26.59 %. Future work will be conducted on the improvement of energy performance.

ACKNOWLEDGEMENT

Financial support provided by the National Natural Science Foundation of China (No. 21636009) and sponsorship from China Scholarship Council (201806440077) are gratefully acknowledged. The research is also supported by Science Foundation of China University of Petroleum, Beijing (No. 2462018BJC004 and 2462018YJRC010).

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