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Perspective

Energy-efficient methods for production methane from natural gas hydrates

Jun Chen, Yan-Hong Wang, Xue-Mei Lang, Shuan-Shi Fan*

Key Lab of Enhanced Heat Transfer and Energy Conservation, Ministry of Education, South China University of Technology, Guangzhou 510640, Guangdong, China

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Gas hydrates now are expected to be one of the most important future unconventional energy resources. In this paper, researches on gas hydrate exploitation in laboratory and field were reviewed and discussed from the aspects of energy efficiency. Different exploiting methods and different types of hydrate reservoir were selected to study their effects on energy efficiencies. Both laboratory studies and field tests have shown that the improved technologies can help to increase efficiency for gas hydrate exploitation. And it also showed the trend that gas hydrate exploitation started to change from permafrost to marine. Energy efficiency ratio (EER) and energy return on energy invested (EROI) were introduced as an indicator of efficiency for natural gas hydrate exploitation. An energy-efficient hydrate production process, called "Hydrate Chain Energy System (HCES)", including treatment of flue gas, replacement of CH_4 with CO_2, separation of CO_2 from CH_4, and storage and transportation of CH_4 in hydrate form, was proposed for future natural gas hydrate exploitation. In the meanwhile, some problems, such as mechanism of CO_2 replacement, mechanism of CO_2 separation, CH_4 storage and transportation are also needed to be solved for increasing the energy efficiency of gas hydrate exploitation.

1. Introduction

Energy plays an important role in the history of human development. Firewood, coal, oil, natural gas and so on are considered as the energy resource for warmth, cooking, automobile and other human activities until now. However, environmental problems associated with the use of the energy also began to appear, and tended to be more serious. One of the ways to solve the contradiction between environmental problems and energy demand is searching for new and clean energy resource.

Natural gas hydrates now are expected to be one of the most important clean energy resources among unconventional resources of coal bed gas, shale gas, biogas, and hydrated gas. Natural gas hydrate is a non-stoichiometric solid, which often forms at lower temperature and elevated pressure. It is known to occur in both terrestrial and marine environments where natural gas and water are present, and where pressure and temperature conditions are in favor of hydrate formation. The amount of methane in the form of hydrate below the ocean floor was estimated to be about 20,000 trillion m^3 in the world [1]. The amount of estimated natural gas hydrates is more than that of all the current fossil fuel energy combined as shown in Fig. 1 [2].

All natural gas hydrate reservoirs can be divided into four categories which can be attributed to Class I, Class II, Class III, and Class IV [4–10]. Class I is the flowable gas–water plus the natural gas hydrate layer, while Class II is the flowable water plus natural gas hydrate layer. Class III was considered as the natural hydrate layer sandwiched between impermeable layers, while Class IV is the low saturated natural gas hydrates distributed in homogeneous strata. A small part of hydrates in arctic can be classified to Class I hydrate as shown at the top of Fig. 2, which can be easily developed. However, large amounts of hydrate were distributed in marine area, which can be classified to Class IV hydrate reservoir with difficulty in exploiting as shown at the bottom of Fig. 2. The recoverable gas hydrate is less than 1/1000 with current technologies and economic feasibility. So, over the long term, to improve energy efficiency plays a major role in ensuring adequate future supplies of natural gas and moderating future energy prices.

One of the methods to improve energy efficiency can focus on the exploited method. Thermal stimulation [11–16], depressurization [17–20], and inhibitor injection [21], are three common methods to exploit natural gas hydrate. New methods, such as replacement of hydrate by CO_2, [22,23], may help improve energy efficiency in natural gas hydrate exploitation. In the meanwhile, new idea is also important for improving energy efficiency during natural gas hydrate exploitation. Energy efficiency ratio (EER) and energy return on energy invested (EROI) can be used as the

* Corresponding author. Tel: +86 2022236581; Fax: +86 2022236581.
E-mail address: ssfan@scut.edu.cn (S.-S. Fan).

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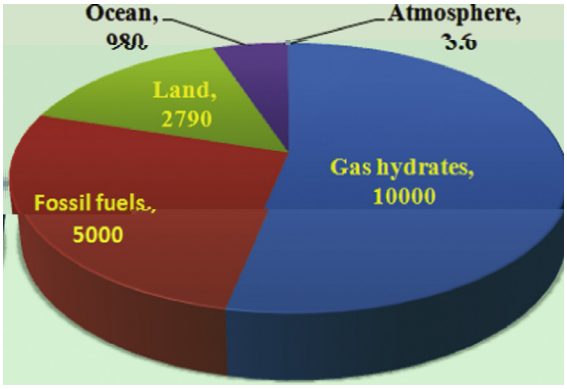

Fig. 1. Modified proportion of organic carbon in various forms from Kvenvolden [2].

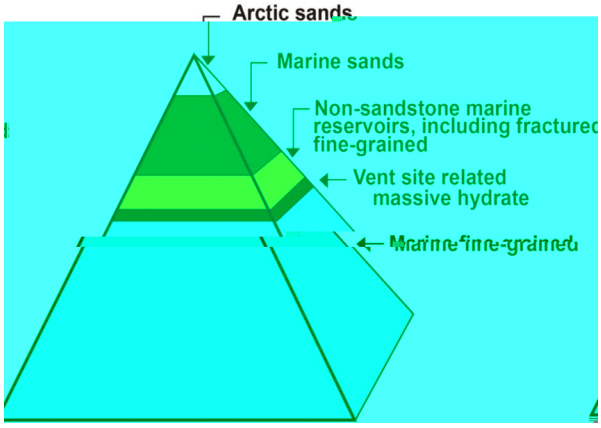

Fig. 2. Gas hydrate resource pyramid from Schoderbek and Boswell [3].

reference to explain the energy efficiency during natural gas hydrate exploitation.

In this paper, progress of gas hydrate exploitation which includes experiments in laboratory and field test was reviewed and discussed from an economic point of view. Energy efficiency ratio and energy return on energy invested were introduced for natural gas hydrate exploitation. Finally, an energy-efficient hydrate production process, called "Hydrate Chain Energy System (HCES)", including treatment of flue gas, replacement of CH_4 with CO_2, separation of CO_2 and CH_4 mixtures, and storage and transportation of CH_4 in hydrate form, was proposed for future natural gas hydrate exploitation.

2. Progress of gas hydrate exploitation

2.1. Research in laboratory

Many countries, including United States of America, Japan, China, Korea, France, Germany, Russia, India and so on are interested in natural gas hydrate exploitation.

In order to simulate gas hydrate reservoir in real environment, different experimental apparatuses have been designed. Yousif and Abass [24] designed an apparatus for gas hydrate dissociation in sediment core. The apparatus which collected a lot of informations about gas hydrate dissociation could be the earliest apparatus to simulate gas hydrate exploitation. Eaton et al. [25] adopted a high pressure reactor to simulate gas hydrate formation and dissociation in the seabed. The volume and rated pressure of the reactor were 72 L and 20 MPa, respectively. Visual window and ultrasonic were used to confirm and analyze gas hydrate formation and dissociation. A 117.8 L pilot scale reactor was set up to conduct three-dimensional synthesis and simulation [26]. Konno et al. [27] have set the world's largest reservoir simulating vessel with the internal volume of 1606 L, which can be more close to gas hydrate reservoir in nature. Except for apparatuses, Rempel and Buffett [28] simulated gas hydrate formation in marine environmental condition by using their vimineous apparatus without stirrer. They first found that gas hydrate can form in natural porous medium without the existence of free gas.

In addition, a lot of properties, such as thermal conductivity [29], phase equilibrium [30], permeability [31], wave velocity [32] have been studied which may help improve energy efficiency for natural gas hydrate exploitation. Other properties are also studied. For example, the mechanical properties of the hydrate structure were tested and the replacement of gas hydrate by carbon dioxide was simulated at Dalian University of Technology [33,34]. Li et al. [35,36] also have conducted a series of experiments to measure physical parameter of gas hydrate.

Gas hydrate formation and dissociation process also plays an important role in gas hydrate exploitation. Yusuke et al. [37] observed CH_4 and Krypton (Kr) hydrate dissociation at the surface of ice using an optical scanning microscopy. They found that ice formation behavior is different with different dissociation methods, which means different methods can change energy efficiency in natural gas hydrate development. A high pressure reactor was used to study gas hydrate formation and dissociation for gas hydrate exploitation in China University of Petroleum (Beijing) [38,39]. The results showed that ice are likely to form at the initial gas hydrate dissociation, and gas hydrate dissociation was controlled by heat transfer. From the results reported by Yoshihiro et al. [40], depressurization-induced gas production can be accelerated in the ice-formation regime. Du et al. [41] have in situ studied gas hydrate formation and dissociation for gas hydrate exploitation in a two-dimensional reactor. Qindao Marine Geological Survey also conducted experiments of hydrate dissociation. They concluded that gas hydrate was easily affected by heat transfer. The heat transfer efficiency of the porous medium is decreased by the center direction. Hydrate dissociation rate and the distance from the heat source is two function attenuation relationship [42–44]. The national energy laboratory of national geological survey of America, University of Columbia also conducted gas hydrate formation and dissociation research [45–47].

Methods to exploit gas hydrate are also very important. Li et al. [48] conducted gas hydrate exploitation by injection of NaCl solution. The temperature and injected rate of NaCl solution were 60 °C, 80 °C, 100 °C and 12 mL/min, 15 mL/min, 18 mL/min, respectively. The results have shown that higher injected rate and temperature made gas production rate higher. However, increased injected rate and temperature would reduce energy efficiency. They thought that depressurization or injection of saline water may be more effective to exploit gas hydrate [49,50]. Mikami et al. [51] have analyzed replacement of CH_4 hydrate by CO_2 and found that formation of CO_2 hydrate would result in replacement process occurring only at the surface, which can prevent further CO_2 replacement process. Masuda et al. [52] have studied exchange ratio by injection of N_2/CO_2 mixtures into hydrate-bearing sediments. Injection rate and pressure are kept in 80 L/min and 7 MPa, respectively. The results have shown that higher exchange ratio existed in lower gas hydrate saturation. Exchange ratios were about 30% and 5% for gas hydrate saturation of 41% and 60%, respectively. They also thought that formation of N_2/CO_2 hydrate can prevent further replacement process. Qi et al. [53] studied the effect of pressure and temperature on the replacement rate by using a self-made gas hydrate device. The experimental results showed that temperature had a great influence on the replacement process. Because carbon dioxide formation condition is milder than that of methane hydrate formation, replacement efficiency can reach 48% at the pressure of 2.5 MPa in their experiments.

Table 1. Natural gas hydrates production in fields[a].

Name	Location	Reservoir type	Method	Year	Production period	Cumulative gas produced (m^3)	Price ($/m^3$)
Messoyakha	Arctic on the border of West Siberia	permafrost Class I	depressurization	since 1970	1970–2011	5.4×10^9	~0.1
Mallik	Northwest of Canada	permafrost Class I	thermal stimulation	2002	5 days	516	56,201.6
			depressurization	2007	12.5 h	830	34,939.8
			depressurization	2008	139 h	13,000	2,230.7
Ignik Sikumi	Alaska north slope	permafrost, Class I	CO_2 replacement	2012	about 6 weeks	24,085	1,204.1
Nankai Trough	Margin of the Daini Atsumi Knoll	marine sand, Class II	depressurization	2013	6 days	120,000	241.7

[a] The data production period and cumulative gas produced were obtained and estimated from literatures [55–59].

2.2. Field production of gas hydrate

All researches for gas hydrate exploitation are aimed in field production of gas hydrate. Field gas production of hydrates is the most direct and effective method to test the feasibility of industrial exploitation of natural gas hydrate. However, most exploitation of natural gas hydrate is only within scientific research because of high technical difficulty, small scale, and some other reasons. Therefore, most of gas hydrate exploitation in field production is short-term, lacking data on the long-term accumulation and has some discrepancy with commercial exploitation. Table 1 shows the natural gas hydrate production in different fields.

Messoyakha gas hydrate field is the only commercial exploitation of natural gas hydrate reservoir. This field is located in permanent permafrost of Siberia and was accidentally discovered in the process of drilling conventional natural gas in 1963. Makogon and Trofim [54] issued a statement in 1964 that first announced the existence of gas hydrate field in nature, which locate in permanent permafrost of Siberia. Since January 1970, the average pressure of gas hydrate reservoir has dropped from 7.93 MPa to 6.07 MPa and collected 5.4×10^9 m^3 natural gas until 2011 from gas hydrate dissociation. If no natural gas hydrate had dissociated, the gas pressure would have fallen to 3.65 MPa, not to 6.07 MPa [55]. The cost was estimated to be the same as conventional gas production.

Mallik region was located in the northwest of Canada, which is in the Arctic environment with favorable conditions for the formation and preservation of natural gas hydrate. Production test of gas hydrate was conducted in 2002 in Mallik region and 516 m^3 of natural gas was obtained in 5 days. Mallik hydrate field was also tested using thermal stimulation and depressurization method in 2007 and 2008, respectively. Tests were conducted to evaluate the natural properties of gas hydrates, and for the first time to measure and monitor their long-term production behavior. About 830 m^3 and 13,000 m^3 of natural gas were acquired in 12.5 h and 139 h from Mallik hydrate field in 2007 and 2008, respectively [56], under the collaboration by exporters from five countries and multiple organization.

Natural gas hydrate production test area in America is located in Alaska North Slope. Production test in Alaska North Slope started in 2003. But, unfortunately, no hydrate layer was found in the test. Mt. Elbert Well in Alaska North Slope test was conducted test in 2007 using depressurization. Injection of carbon dioxide and nitrogen to exploit natural gas hydrate was conducted Ignik Sikumi and about 24,085 m^3 of natural gas was acquired in 2012 [57].

Gas hydrate exploitation in Japan started early, and has got much attention and support from enterprises and the government. Japanese business community also participated in the international exploitation of gas hydrate actively, and has put a lot of human resources to participate in the Canadian Mallik hydrate reservoir exploitation and the United States Alaska carbon dioxide replacement exploitation.

From Table 1, one can know that permafrost is the first choice for natural gas hydrate exploitation. Messoyakha succeeded in commercial exploitation of natural gas hydrate reservoir and can be classified to Class I. This illustrates that natural gas hydrate reservoir in Class I can provide economic benefit under existed technologies. From three gas hydrate exploitation tests in Mallik, depressurization method may be more economic and can provide higher energy efficiency than thermal stimulation because 830 m^3 of natural gas was obtained in 12.5 h by depressurization with the estimated price of 34,939.8 $/m^3$ natural gas and only 516 m^3 of natural gas was obtained in 5 days by thermal stimulation with the estimated price of 56,201.6 $/m^3$ natural gas in 2007 and 2002, respectively. Estimated price of gas production from hydrate reservoir in 2008 is lower than in 2007, may ascribe to the use of stepwise reduction of the bottom hole pressure. So, new method will improve the energy efficiency of gas hydrate exploitation. In 2013, Japan succeeded in collecting natural gas from offshore seabed in Nankai Trough with the estimated price of 241.7 $/m^3$. About 20,000 m^3 per day of natural gas was collected in 6 days, which have good consistency with their early numerical simulation of gas production [58]. It was the first offshore gas production from hydrate in Japan and there is a trend that gas hydrate exploitation change from Class I to Class II, Class III, and Class IV, which finally let gas hydrates become the new sources of energy.

3. Problems and challenge for gas hydrate exploitation

3.1. Energy efficiency

Energy efficiency is important for gas hydrate exploitation. For Thermal stimulation, EER can be defined as following equation:

$$\mathrm{EER} = \frac{H_{\mathrm{combustion}}}{H_{\mathrm{dissociation}}} \tag{1}$$

where, heat combustion of natural gas ($H_{\mathrm{combustion}}$) is 890 kJ/mol, dissociation enthalpy of natural gas hydrate ($H_{\mathrm{dissociation}}$) is 51.3 kJ/mol. In theory, EER in thermal stimulation dissociation of hydrate is 17.3. For injection of inhibitor, temperature shifted by inhibitor was 0.42 °C per 1 wt % within 3–5 wt% dosage of inhibitor, which indicated that injection of inhibitor may not be used alone. For depressurization,

$$\mathrm{EER} = \frac{H_{\mathrm{combustion}}}{H_{\mathrm{dissociation}}} = \frac{H_{\mathrm{combustion}}}{T\Delta V \frac{\mathrm{d}P}{\mathrm{d}T}} \tag{2}$$

where, ΔV is corresponding volume change, dP and dT are the phase equilibrium points along the appropriate three-phase line. EER of depressurization is related to the scale of exploration. Depressurization method may be the most energy efficient method. For carbon dioxide replacement, formation enthalpy of CO_2 hydrate is 57.98 kJ/mol, while dissociation enthalpy of natural gas hydrates ($H_{\mathrm{dissociation}}$) is 51.3 kJ/mol. So, the total energy consumed during replaced process is −6.68 kJ/mol, which indicated carbon dioxide replacement can spontaneously occur. Different energy efficiency and prices may be obtained using different method. In addition, energy efficiency and

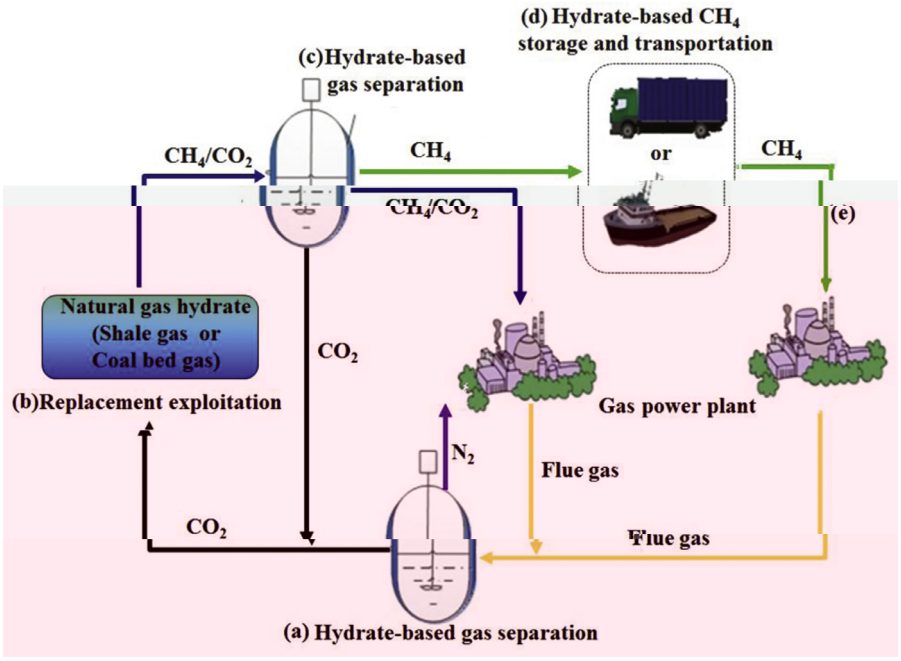

Fig. 5. Hydrate Chain Energy System: a energy-efficient production methane from natural gas hydrates combined with CO_2 and N_2 separation. HCES: (a) and (c) is gas mixtures separation process by formation of gas hydrate; (b) is the replacement process; (d) is CH_4 hydrate formation process for CH_4 transportation; (e) is gas hydrate dissociated process for gas power plant.

(HCES)" process was proposed for future natural gas hydrate exploitation and the schematic diagram is shown in Fig. 5.

The first time of hydrate formation/dissociation process is to deal with waste gas, such as flue gas collected from gas power plant as shown in Fig. 5(a). Relatively pure CO_2 can be obtained through gas hydrate formation/dissociation process, and can be used to exploit natural gas hydrate in the second hydrate formation/dissociation process as shown in Fig. 5(b). It can isolate CO_2 in marine by the formation of hydrate and obtain gas mixtures (mainly contain CH_4 and CO_2) from gas hydrate dissociation as shown in Fig. 5(b). Of cause, CO_2 exploited process can also be used for shale gas and coal bed gas exploitation as shown in Fig. 5(b). Gas mixtures obtained from exploited process can be separated and obtained relative pure CH_4 through the third hydrate formation/dissociation process as shown in Fig. 5(c). The obtained CH_4 can be transported by formation of hydrate in the fourth hydrate formation process as shown in Fig. 5(d) and finally used for gas power plant by dissociation of hydrate as shown in Fig. 5(e). Gas mixtures (mainly contain CH_4 and CO_2) acquired from separated process as shown in Fig. 5(c) can also be used for gas power plant. So, a virtuous circle for energy utilization is obtained using HCES process. However, energy efficiency (EER, EROI) needs to be improved for the proposed process. For example, flue gas can be considered to replace natural gas hydrate directly without separation as shown in Fig. 6.

Except for optimization of the whole circle in gas hydrate exploitation, some problems also need to be solved for increasing the

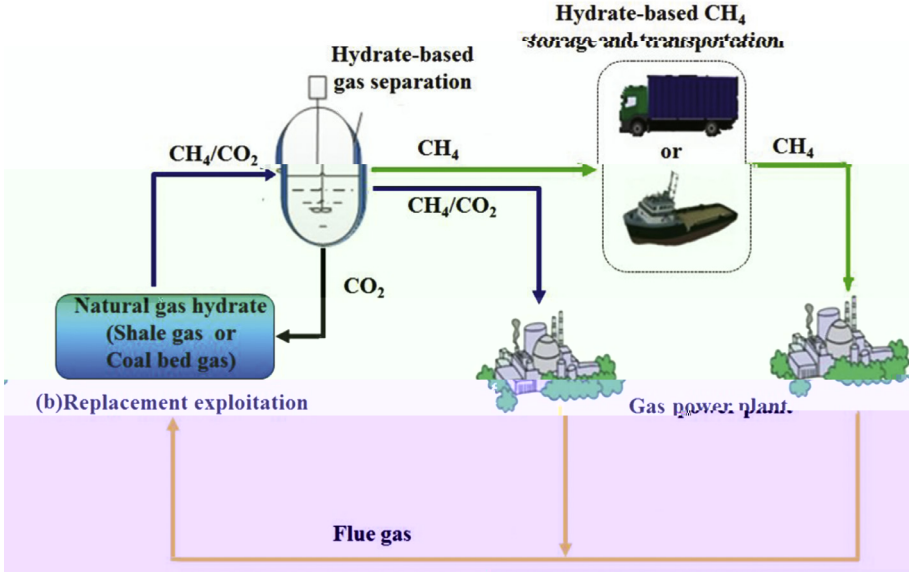

Fig. 6. A new approach to produce methane from non-conventional resources such as hydrates, shale gas, and coal bed gas. This process is called "flue gas replacement/hydrate-based separation/NGH storage and transportation".

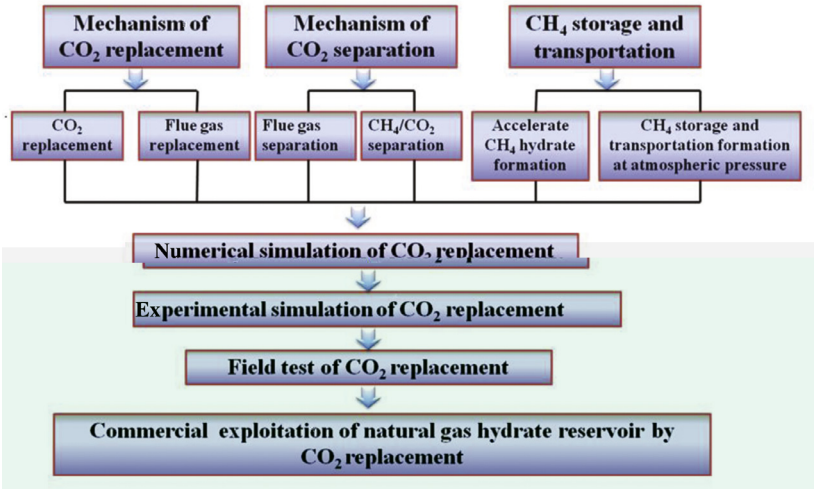

Fig. 7. Future researches on gas hydrate exploitation.

energy efficiency to realize the method and the schematic diagram was shown in Fig. 7.

From Fig. 7, one can know that mechanism of CO_2 replacement, mechanism of CO_2 separation, CH_4 storage and transportation need to be studied for improving the energy efficiency of gas hydrate exploitation. For mechanism of CO_2 replacement, both pure CO_2 replacement and flue gas replacement should be considered. Flue gas separation and CH_4/CO_2 separation should be studied for mechanism of CO_2 separation, while CH_4 hydrate formation rate and CH_4 storage and transportation at atmospheric pressure should be studied for CH_4 storage and transportation. In the meanwhile, numerical and experimental simulation of CO_2 replacement, field test of CO_2 replacement should also be pushed forward before the final realization commercial exploitation of natural gas hydrate.

HCES proposed in this work not only can help improve energy efficiency for natural gas hydrate exploitation, but also for shale gas and coal bed gas exploitation. Other hydrate-based technologies, such as gas mixtures separation, gas storage and transportation can also be improved with the progress of the proposed HCES.

4. Conclusions and prospects

In this paper, energy efficiency for energy resource potential of gas hydrates was discussed. Some conclusions and prospects are as follows:

(1) Lab studies on gas hydrate exploitation were introduced about apparatuses, properties, hydrate formation and dissociation process, and exploitation methods. With better understanding of the properties, hydrate formation and dissociation process, improved methods can increase energy efficiency for gas hydrate exploitation.

(2) Most of field productions of gas hydrate are conducted in permafrost. However, there is a trend that gas hydrate exploitation change from Class I to Class II, Class III, and Class IV, which finally makes gas hydrates become the new sources of energy.

(3) Energy return on energy invested was introduced and suggested to be used as an indicator of efficiency for natural gas hydrate exploitation. HCES, which included treatment of water gas, CO_2 replacement, CO_2 separation, and CH_4 storage and transportation, was proposed for future natural gas hydrate exploitation.

Acknowledgments

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