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Comparative Study on Recovery of Methane Gas from Natural Gas Hydrates Using Combination of Depressurization & Thermal Simulation Methods

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ABSTRACT

One of the cleanest burning fossil fuels is natural gas and is recognized as a strong candidate for energy resources as compared to oil and gas. Natural gas hydrates are commonly found in Shallow and deep waters where suitable pressure and temperature condition combine to make it stable. Gas Hydrates are the potential source of methane which needs to be extracted from the seabed but exploitation of it is much far from being economically viable and safe. Various methods for the exploitation of methane gas are depressurization, thermal stimulation, chemical inhibitor injection and replacement methods. These methods are being widely studied by using experimental approach and numerical methods. Numerous Fields tests carried out by different nations to produce the methane gas from natural gas hydrate reservoir and observed that it's a complex process. This paper gives comparative study on the effect of exploitation methods on methane gas recovery from natural gas hydrate deposit. Combination of different methods for the production of methane gas from natural gas hydrate is briefly reviewed. Possible methods for the extraction of natural gas in each method and challenges/limitations are discussed in detail. Combination of thermal stimulation and depressurization method is observed to be more efficient than the individual methods in terms of recovery of methane gas from gas hydrates.

Keywords: Natural Gas; Natural Gas Hydrates; Clean Energy; Depressurization; Thermal Stimulation; Methane Recovery.

1. INTRODUCTION

There has been a constant increase in demand for energy supply over the past few decades and this has resulted in great exploitation of the fossil fuels (Behera and Dash, 2017). Reports have shown that global energy demand and consumption will rise over the upcoming few decades, contributors being developing countries like India and China, it might increase over 110% till the year 2040 (U.S. Department of Energy Washington, 2021). Energy resources are necessary for social and economic development for the nations. Developments in renewable and nuclear resources can provide potential alternate against fossil fuels. However, numerous studies have shown that these resources would not meet the required energy demands for a longer period of time in the context of future needs. For the upcoming decades, more than 70% of energy will be provided by the fossil fuels despite the growth of renewable and nuclear energy resources (U.S. Department of Energy Washington, 2021). Almost 75-80% demand for natural gas globally is satisfied by the conventional resources, but over the recent years, the unconventional resources like coal bed methane, shale gas, tight gas and natural gas hydrates has become the area of interest for many researches/scientist (World Energy Outlook 2020 – Analysis - IEA, 2020).

Unconventional resources have grabbed a lot of attention in the past few years because of their massive reserves. Natural gas hydrates (NGH) being one of them, can be considered as potential source of future energy requirements because of their vast existence and huge reserves of methane gas trapped inside them (Pandey et al., 2017a, 2017b; Zhao *et al.*, 2017). Gas hydrates have been considered a great alternative that provides clean energy with high energy density (Kong *et al.*, 2018). If exploited cautiously, gas hydrates could be a feasible clean energy resource for upcoming years (Zhao *et al.*, 2017) and play a vital role in transportation of clean energy in the form of hydrate slurries in oil and gas industries (Pandey et al., 2017a; Pandey and Sangwai, 2020a, 2020b).

Development and growing population have led to increase in energy demands which has brought the attention towards the potential methane gas trapped inside the hydrates. These gas hydrates have a very diverse geographical distribution of reserves under ocean subsurface, permafrost regions and coastal environment. Globally, estimation of these hydrates almost twice the conventional resources alone or even greater than the conventional and other unconventional resources combined (Demirbas *et al.*, 2016).

This paper provides a review of different methods of production of natural gas from Natural gas hydrates. These methods are still being experimented on in the laboratories and exploitation trials have only been conducted by a few countries among which Messoyakha gas field is the only to have carried out the commercial production (Makogon and Omelchenko, 2013). Comparative study of combination of thermal stimulation method and depressurization method has been provided to give an overview to the readers. This paper also reviews the structure and properties of natural gas hydrates to provide profound information to the readers.

2. GAS HYDRATES

NGH are crystalline water-based complex structured compounds that physically resembles ice and also known as fire ice/burning ice (Sloan and Koh, 2007). Natural gas molecules are trapped inside the caged structure of hydrogen bonded frozen water molecules. In cage like structure, the water molecule act as host molecule and any natural gas trapped inside the cage structure act as guest molecule. These are formed under suitable hydrate formation conditions usually high pressure and low temperature (Koh *et al.*, 2011; Pandey *et al.*, 2018). The main reason for the existence of gas hydrate is the ability of water molecules to form a lattice structure through hydrogen bonding under suitable conditions. The lattice structure formed by thermodynamically. So, the water molecules attract non-polar gas molecules into the cages to make the hydrate structure stabilized under favorable forming conditions of hydrate (Koh *et al.*, 2011). Therefore, gas hydrates can form at temperatures above the freezing point of liquid water (Bishnoi and Natarajan, 1996).

2.1 Structure of NGH

NGH usually form three types of crystallographic structures, two of them belongs to cubic group that are structure I (sI) and structure II (sII) and the third one belongs to hexagonal group called structure H (sH). The structures of natural gas hydrates are shown in **Figure 1**. Unit cell of sI has 46 H_2O forming cages of 2 types, small and large among which 2 are small cages and 6 are large ones. Small cage is pentagonal dodecahedron (5^{12}) and large one is tetradecahedron, specifically hexagonal truncated trapezohedron (5^{12} 6^2). Typically, in sI, guest molecules are ethane, CO_2 and CH_4 gases. sII consist of 136 H_2O forming cages of 2 types, small and large among which 16 small cages and 8 large one. The small cages are pentagonal dodecahedron (5^{12}) and large one is hexadecahedron ($5^{12}6^4$). In sII, guest molecules are propane, iso-butane, O_2 and N_2 gas. sH consist of 34 H_2O molecules forming 3 types of cages among which are 2 cages of different types and 1 large cage. Unit cells consist of 3 small cages of 5^{12}, other 2 small cages of $4^35^66^3$ and one large of $5^{12}6^8$. Guest molecules are methane + neohexane and methane + cycloheptane (Sloan and Koh, 2007).

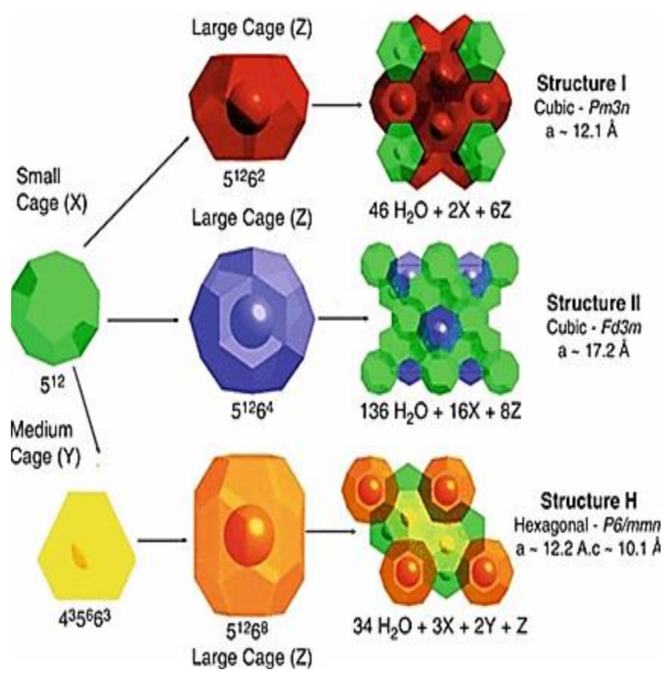

Figure 1. Structures of natural gas hydrates (Kumar and Linga, 2018).

2.2 Properties of NGH

All the three structures (sI*,* sII and sH) of NGH are approximately 85% water and 15% gas, hence the physical properties of NGH are pretty similar to ice except the properties like thermal conductivity and thermal expansivity (Sloan, 1998). Value of thermal conductivities of NGH have been studied in many experimental studies and have been found to be almost 5 times lower than that of ice at melting point. Thermal conductivity of NGH does increase to a small extent with increasing temperature (Gabitto and Tsouris, 2010).

Guest to cavity size ratio in the structure of hydrate plays an important role in determining physical properties of the NGH. Guest molecules needs to be in a particular size range to make the structure stabilized. In sI*,* it needs to be below 0.35 nm and in sII, it needs to be above 0.75 nm to be stabilized. Larger guest molecules are usually the ones to determine the structure of NGH (Sloan, 1998). The size ratio of the guest molecules within the host cages sets the phase equilibrium and the three phase (liquid water + NGH + gas) equilibrium pressure exponentially depends on the temperature (Gabitto and Tsouris, 2010).

3. GAS PRODUCTION METHODS

3.1 Thermal Stimulation

Thermal stimulation methods is a simpler process to extract the gas from hydrate cages. Natural gas hydrates are heated *insitu* reservoir till temperature where its local temperature is away from the stability region of hydrates and hydrates become unstable (Chong *et al.*, 2016). Once the hydrate is dissociated, the gas entrapped in the lattice is released which can be recovered from the wellbore (Nair *et al.*, 2018).

3.2 Depressurization

In depressurization method, the pore pressure of natural gas hydrate reservoirs is reduced by drilling process. Afterwards, the reduced pressure of hydrate cages below the hydrate dissociation equilibrium pressure-temperature conditions. Energy required for gas production by depressurization techniques is lesser than thermal stimulation method. (Wang *et al.*, 2018; Yang *et al.*, 2019).

3.3 Chemical inhibitor injection

Chemical inhibitor injection method for gas recovery hasn’t implemented at laboratory scale and field tests. Chemical inhibitor injection works on the principle of shifting phase equilibrium curve toward lower temperatures and higher pressures, by which hydrates get unstable at natural conditions (Liang *et al.*, 2020). Mainly there are two types of inhibitors, thermodynamic inhibitor and kinetic inhibitor (Mech et al., 2015a, 2015b; Chong *et al.*, 2016). Thermodynamic inhibitor alters the equilibrium condition of hydrates and kinetic inhibitor slows down the rate of formation of hydrates (Xu and Li, 2015; Pandey *et al.*, 2019). For gas production, thermodynamic inhibitor is of particular interest due to increase in no hydrate stability zone. Commonly used thermodynamic inhibitors are methanol, ethylene glycol etc. (Liang *et al.*, 2020).

3.4 Replacement methods

In replacement method, methane gas molecule is replaced by injecting other gas components into natural gas hydrate reservoirs. (Chong *et al.*, 2016). Generally, CO_2 gas is injected because CO_2 hydrates are favorable to form *insitu* hydrates and more stable. CO_2 hydrate formation is exothermic process which indicates that the heat released is more than required heat for CH_4 hydrate disintegration process (Xu and Li, 2015).

3.5 Combination of thermal stimulation and depressurization

Each of the recovery techniques discussed above have their limitations, it is widely agreed that combination of different techniques enhances the effectiveness of gas production rate (Wang, Feng and Li, 2019). One of the techniques, combination of thermal stimulation and depressurization in a single vertical well by huff and puff method (Nair *et al.*, 2018). Numerous cycles of hot fluid injection, soaking and gas production are involved in huff and puff method (Song *et al.*, 2015). In pilot-scale hydrate simulator (PHS) of volume 117.8 L using huff and puff method, a large scale of gas production study was carried out. This study justifies the economic feasibility of huff and puff method (Wang, Feng and Li, 2019).

4. COMPARATIVE STUDY

Extensive studies for natural gas extraction are reported in **Table 1** in order to compare the combination methods with individual extraction methods. Corresponding outcomes of these studies are listed in **Table 2**. Experiments have shown good results of gas extraction by using various methods of exploitation of natural gas hydrates (Song *et al.*, 2015).

Table 1: Extensive studies conducted to compare the combination method with individual extraction methods.

Extensive Research	Methods	Research Inferred
(Nair *et al.*, 2018)	Energy recovery from simulated clayey gas hydrate reservoir using depressurization by constant rate gas release, thermal stimulation and their combination	The extraction of methane from hydrate reservoirs using depressurization methods is widely discussed. In addition, effect of clay minerals in hydrate bearing sediments is enlightened.
(Wan *et al.*, 2018)	Heat transfer analysis of methane hydrate dissociation by depressurization and thermal stimulation methods	The behavior of three-dimensional heat transfer during dissociation of hydrates by thermal stimulation and depressurization based on the experiments in a cuboid pressure vessel (CPV) is studied.
(Wang *et al.*, 2018)	Evaluation of thermal stimulation on gas production from depressurized methane hydrate deposits	The reaction of hydrate dissociation induced by depressurization in coexistence with thermal stimulation is investigated. In addition, profiles of pressure, temperature, gas production rate and cumulative gas production during the production of gas are analyzed.

Table 2: Results of hydrate dissociation using depressurization, thermal stimulation and combination of depressurization & thermal stimulation.

Method	Saturation (%)	Production Time (min)	Total gas production (mL)	Average rate of gas production (mL/min)	Percentage of gas production (%)
Depressurization	31.90	62.7	73.77	1.18	45.20
	41.31	84.8	106.56	1.26	52.00
	51.61	93.9	130.21	1.39	56.24
Thermal Stimulation	31.90	84.1	46.17	0.83	28.29
	41.31	129.2	68.28	0.71	33.32
	51.61	158.1	101.13	0.70	43.68
Combination of depressurization and thermal stimulation	31.90	52.5	80.07	1.53	49.06
	41.31	82.5	127.02	1.54	61.99
	51.61	89.7	173.33	1.93	74.87

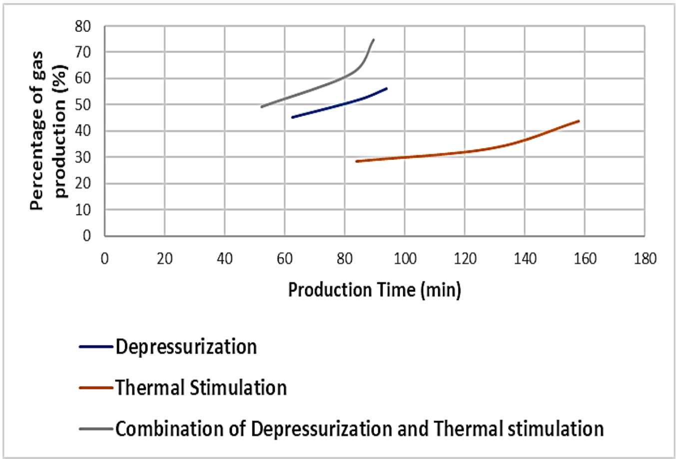

Figure 2. Percentage gas production v/s time using different production methods.

Figure 2 represents the comparative performance analysis between combination method and individual extraction method. Studies reported that a better and promising result after applying thermal stimulation and depressurization method together (Nair *et al.*, 2018). Data reported from the individual extraction method and combination of these two methods are compared for the better understanding from the perspective of recovery of natural gas from hydrates.

5. CONCLUSION

In this paper, the behavior of gas production from natural gas hydrate deposits by using different methods has been discussed. Depressurization is reported as the most energy efficient methods, but it gives low production rate. On the other hand, thermal stimulation and chemical injection requires more energy in order to heat the injection fluid and pump the inhibitor into the hydrate sediment. However, the combination of thermal stimulation and depressurization method is observed to be more efficient against individual methods. The combined method improves the production rate and the overall efficiency in terms of total production of natural gas along with the average rate of production gas and percentages of gas production.

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