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Techniques for Exploitation of Gas Hydrate (Clathrates) an Untapped Resource of Methane Gas

Amit Arora[1], Swaranjit Singh Cameotra[2]* and Chandrajit Balomajumder[1]
[1]*Department of Chemical Engineering, Indian Institute of Technology, Roorkee, India*
[2]*Institute of Microbial Technology, Chandigarh, India*

Abstract

Methane gas hydrates is unique source of methane gas in which gas is caught in crystalline ice like structure in permafrost regions and under the sea. The total amount of carbon present in this unique source far exceeds the conventional fossil fuels. This article briefly describes understanding of methane hydrates, their origin, occurrence, energy potential and their exploitation by techniques like depressurization, thermal stimulation, inhibitor injection, co2 sequestration, microwave technology, microwave and fluorine gas technology.

Keywords: Methane hydrate; Carbon content; Energy resource; CO_2 sequestration; Microwave and fluorine gas technology

Introduction

Gas hydrates are non-stichiometric compounds formed by gases like CH_4, C_2H_6, and CO_2 etc. when they come in contact with water at lower temperature and higher pressure. There is no chemical reaction between them it is just intermingling of two compounds. In nature they are found in sea water and in permafrost regions and are seen as future fuels. Thermodynamically, their formation is favoured at lower temperature and higher pressure [1,2]. Such conditions are met in ocean-bottom sediments at water depths down 500 m [3]. One volume of gas hydrates can discharge about 160 volumes of methane and 0.8 volume of fresh water at standard temperature and pressure (STP). Gas hydrates are considered as tremendous reserve of natural methane in the earth [4,5]. With pressurization, gas hydrates can remain stable at temperatures up to 291 K. Density of gas hydrae is 0.79 kg/L [6].

The worldwide organic carbon in the gas hydrates is far more than the carbon content in total fossil fuel [7-9].

Occurrence and distribution

It is estimated that the amount of methane in the form of clathrate at the bottom of the oceans is about 6.4 trillion tons. [10]. Clathrate hydrates occur naturally on Arctic permafrost and submarine continental margins [3,5,11,12]. These are present in oceanic sediments along continental margins as well as in polar continental settings [13-16]. Methane found within the marine sediments can be either biogenic [17] or thermogenic [18] or both of them. Clathrates are formed as per the following reaction:

$$G+N_H H_2O=G.\ N_H H_2O$$

G is the guest molecule which is methane occurs most abundantly in natural hydrates [19-21]. NH is the hydration number i.e., average number of water molecules per guest molecules in a unit cell of crystalline gas hydrate compound.

The gas hydrates synthesized in the lab is as shown in Figure 1.

Energy potential

There is uncertainty on the amount of methane caught in gas hydrates. The idea given by the studies in pre-1990 of the amount of methane caught in global gas hydrates deposits of the amount of methane trapped in global gas hydrate deposits were in the range from ~10^{17} ft^3 or 10^5 trillion cubic feet [TCF] [22] to 10^8 TCF [23]. With the same period, Kvenvolden (1988) [24,25], Gornitz et al. [26], and Harvey et al. (1995) [27] has also gave similar ideas. In the mid 1990 numerical modelling, evaluation have given the total volume of gas sequestered in gas hydrates from 1.4 to 1.7×10^5 TCF [28,29] to 4.2×10^6 TCF [30] with some intermediate estimates [31] In the most recent review on the concerned, subject Boswell et al. (2011) [32] estimate of 10^5 TCF of methane caught in gas hydrates (gas-in-place or GIP), USA department of energy has said that if only very very less amount of methane stored in hydrates can be exploited. It is almost more than the current supply of natural gas in the country [33,34]. It was mentioned that the energy potential of methane hydrates is greater than that of the other unconventional [35]. Gas hydrates will be a source of attention till their development potential is assessed [36]. Methane hydrates are

Figure 1: Gas hydrate synthesized in lab by our group.

***Corresponding author:** Swaranjit Singh Cameotra, Institute of Microbial Technology, Chandigarh, India, Tel: +91-9041036750; E-mail: ssc@imtech.res.in

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Parameter	Thermal Stimulation Method	Gas Extraction method Depressurization	Conventional gas production
Investment in millions of Rs.	254200	166000	157500
Annual cost in millions of Rs.	160000	125500	100000
Total production(million m^3/year)	1274.26	1557.43	1557.43
Production cost (Rs./million m^3)	6356.6	4025.9	3213.6
Break-even wellhead price (Rs./million m^3)	7945.8	2532.3	3972.9

Table 1: Economics of various dissociation processes [38].

assumed upcoming source of hydrocarbon energy and will be a future fuel [37,38].

Current Techniques of Extraction of Gas from Natural Gas Hydrates

The natural gas from gas hydrate can be produced via depressurization, chemical inhibitor injection and thermal stimulation which have been discussed in literature their economics is as shown in Table 1

Novel Techniques of Extraction of Gas from Natural Gas Hydrates

The conventional techniques have various disadvantages as discussed above, so there is a motivation of inventing a technology which is more efficient, more economical and more green. Various techniques are being studied at lab scale like gas exchange (CO_2 sequestration), microwave technology, Fluorine gas and microwave technology but these need to be investigated in detail before going for commercial productions. These are explained as per the following details:

Gas exchange (CO_2 sequestration)

This technique exploits the greater solubility of CO_2 in water to displace natural gas and hence it achieves the two positive results in a single process i.e., extraction of natural gas from gas hydrates and removal of CO_2 from atmosphere. The gas exchange between CO_2 and CH_4 was first proven in lab by Ohgaki et al. [39], Ohgaki et al. [40]. The experiment observed there is a preference for CO_2 clathrate over. CH_4 in hydrate phase. Not only equilibrium consideration but the heat of CO_2 hydrate formation (-57.9 kJ/mol) is more than the heat of dissociation of CH_4 (54.5 kJ/mol), which is favoring for the natural exchange of CO_2 with CH_4 hydrate, because the above change process is exothermic [41]. Multiphase exchange of CO_2 for CH_4 was given by Hirohama et al. [42]. The author claimed much more rapid CH_4 recovery using gaseous N_2. A mixture of CO_2 and N_2 can also be tried for exchange with CH_4 from gas hydrate. The technology of gas exchange is shown as per the following (Figure 2).

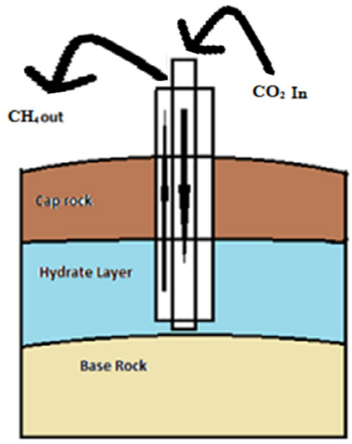

Figure 2: CO_2 sequestration method.

Microwave technology

In conventional heat transfer processes, energy is carried to the material via convection, conduction and radiation because of thermal gradients. But, in microwave energy is passed directly to materials through their molecular interaction with the electromagnetic field. Microwave heating is the change of electromagnetic energy to thermal energy. Microwaves can pass through materials and deposit energy; heat can be created throughout the volume of the material. So, it can decrease processing times and prove to be energy efficient [43]. Petroleum industry has used microwave irradiation recently [44-46].

The exploitation of natural gas hydrate (NGH) for the recovery of gas since possible via heating and microwaves are also gaining attention as heating media in oil and gas industry. The decomposition of hydrates with microwaves were studied by Rogers [47]. While this experiment, the power of microwave was increased gradually. The results showed that microwave heating was very prominent method for hydrate dissociation. Other groups reported experimental studies on the dissociation of propane hydrate by microwave are Fatykhov et al. [48]. The kinetics of methane hydrate crystallization using molecular dynamics simulation in the presence of microwave is reported by English et al. [49]. It was concluded that NGH will dissociate when the intensity was more than a certain value, because the movement of the molecules in the system was increased by microwave.

Advantages of gas hydrate decomposition using Microwave:

Based on the literature review on use of microwave in gas hydrate following advantages are found:

Firstly water is heated by microwave which heats hydrates and dissociates the hydrates and this phenomenon of bulk heating leads to high decomposition efficiency.

Decomposition water created while the hydrate decomposition enhances hydrate decomposition, and the decomposition water and microwave have a synergic effect on the hydrate decomposition.

Gas hydrate can be decomposed dissociated soon with microwave. The more the power is, the greater the decomposition rate is. However, there is a heat efficiency issue generated from the more system temperature.

The microwave heating results into very soon decomposition of gas hydrate compared to other methods.

The studies revealed that the difference of dielectric properties

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within the components may result in temperature difference in the system while the gas hydrates decompose. The hydrate decomposition with microwave is a joint effect of numerous mechanisms.

With the same pressure, microwave can enhance the phase equilibrium temperature.

While the microwave radiation, there is a linear relationship between temperature and time. The rate of hydrate dissociation increases with increasing microwave power.

The energy ratio of microwave heating is more than that of water bath heating, but it is lower than the theoretical value of thermal stimulation production.

Selective heating is possible with microwave. Microwave also increases permeability and porosity.

Keeping into view the above advantages a novel technology like fluorine gas and microwave technology have been proposed explained as below:

Flourine gas and microwave technology

In this method a micro strip antenna with huge power gain and is inexpensive is used with wire line, the tool is placed in well bore and a frequency of 2450 MHz is generated which melts the gas hydrate into water and methyl radical which destabilises the thermodynamic condition and after this fluorine is injected which results into halogenations which is strongly exothermic and releases -431 KJ/mol and methyl fluoride is soluble in water and the solubility is 166 cc per 100 ml of water. This pressurised gas can be obtained via tubing from production well. After this by applying Wurtz reaction, electrolysis and cracking, methane can be recovered. This method enjoys the advantage of green technology because methyl fluoride is eco-friendly. No extra heat is introduced into the reservoir. The diagram of this technology is shown Figure 3.

Environmental Impact of the Use of this Energy Source

The latest research going on in the field of exploitation of this resource of energy is through CO_2 sequestration, hence this energy source can be obtained by dumping CO_2 in sea which will help in reducing global warming. The only threat which is involved is the controlled release of methane from the gas hydrates while CO_2 Sequestration for which lot of research is going on. Even if it is

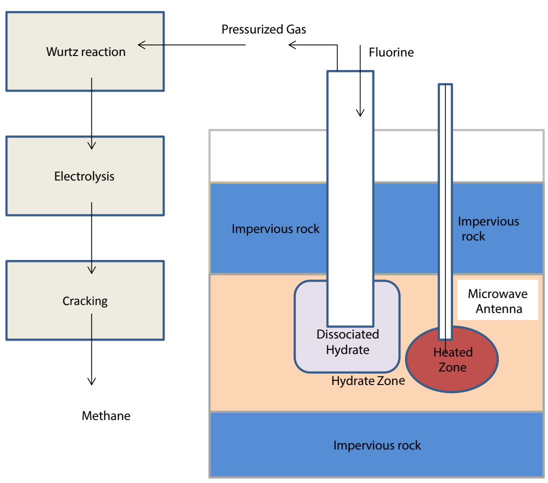

Figure 3: Gas extraction using the microwave technique [50].

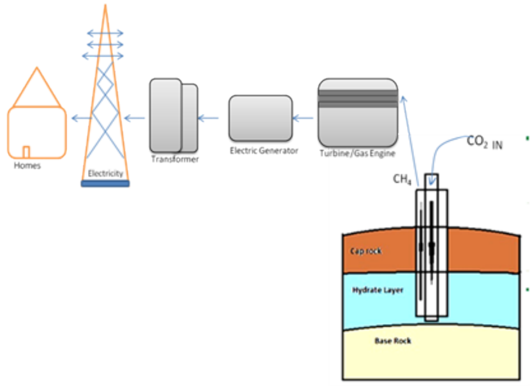

Figure 4: Gas exchange.

dissociated in uncontrolled manner much of methane from dissociated gas hydrate will never reach the atmosphere, rather it may be converted to CO_2 and sequestered by biosphere and hydrosphere before reaching the hydrates. Moreover While combustion of methane 25% lesser CO_2 is released in comparison to when the same mass of coal is combusted and moreover methane don't emit the nitrogen and sulphur oxides which makes it more environment friendly.

Energy Efficiency Benefit Cost of using Methane Hydrates

Almost $500 Billion of US economy is used for fuel. The consumption of energy is expected to increase which will generate the extra demand for the crude oil which is already getting consumed at a faster rate. The amount of methane hydrate is enormous and if very less of methane hydrate can be exploited it can meet the energy demands for centuries. Gas hydrates will be new kind of source of natural gas. The global gas hydrate reserves are almost 100 times more than the natural gas reserves in the world at present [50]. If we are able to exploit only 10% of the gas hydrates reserves it can help in meeting the energy requirements for 600 years [51].

Use of Methane Hydrates in Electricity Generation and Direct Use

There is shift going on from coal based power generation to gas based power generation because of enormous benefits, so in the current context gas hydrates can be directly used for the power generation using CO_2 Sequestration and *in situ* combustion also. The schematic line proposed diagram for the production of electricity from methane hydrates is as shown in Figure 4.

Conclusions

An enormous amount of methane is available in the gas hydrates. Even a small percentage of which could meet the energy requirements of the world for centuries. Long term production test are going on in USA and Japan to make the production viable. Many techniques have been discussed in this paper. However, there is a strong need to prepare a suitable viable economic and green commercial technology for exploiting this untapped energy resource.

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