

## Natural Gas Hydrate (Clathrates) as an Untapped Resource of Natural Gas

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### Abstract

Rapid growth in energy demand, coupled with the worry of anthropological discharge of CO<sub>2</sub> into the environment has seen unusual growth in consumption of natural gas. Exhaustion of conventional reserves of fossil fuel has resulted in the rise of their price which has led to exploitation of novel resources through modern technologies. Methane gas hydrates is one such source of methane gas which is captured in crystalline ice like structure in permafrost regions and under the sea in outer continental margins. It is evaluated that total amount of carbon in the form of methane Clathrate is far more than the carbon content in all the fossil fuel reserves put together and hence these are seen as the future potential energy resource. CO<sub>2</sub> capturing is gaining high attention being a major greenhouse gas. CO<sub>2</sub> Sequestration of gas hydrates can take out methane from Gas hydrates and can reduce the global warming by achieving two objectives of giving new resource of energy methane the burning fuel by reducing pollution.

**Keywords:** Gas hydrate; Methane clathrate; Carbon content; Energy resource; CO<sub>2</sub> sequestration

### Introduction

Today gas hydrates are known as one of the potential source of methane and therefore it is sometimes called as fuel of the future. Gas hydrates (clathrate) are basically a solid and nonstoichiometric crystalline compound made up of water and low molecular weight hydrocarbons. In a clathrate, water molecule called host, arranges itself in a cage like formation that encapsulates a gas molecule known as guest molecule. At certain temperature and pressure condition, these guest and host interact with each other through Vander Waal's interaction and thus stabilize the structure; there is no chemical bonding between the two. When the guest molecule is methane, it is said to be a methane hydrate. It is found in the oceanic and polar sediments where lower temperature and higher pressure is prevalent. Hydrate is considered as condensed water phase at high pressure and low temperature [1]. Such conditions are met at a water depth down to 500 m [2]. Gas hydrates represent a tremendous reserve of natural methane in the earth [3,4]. Density of gas hydrate is 0.79 kg/L [5]. The worldwide organic carbon in the gas hydrates is estimated to be roughly about 10000 × 10<sup>15</sup> grams which is almost double the carbon content in total fossil fuel of the world [6-8]. The global resources of gas hydrates are released recently by Hydrate Energy International (HEI) as a part of global energy assessment conducted by International Institute for Applied System Analysis (IIASA) has given Calculated gas in-place in hydrate bearing sediments, Total Median=43,311 tcf [median, tcf (trillion cubic feet)] [9,10].

### Techniques for Extraction of Gas from Natural Gas Hydrates

The natural gas from gas hydrate can be produced via depressurization, thermal stimulation, chemical inhibitor injection, and CO<sub>2</sub> sequestration. The CO<sub>2</sub> Sequestration is a green technology which consumes the green house gas like CO<sub>2</sub> and gives an energy resource in return which is explained below:

### Latest Research for Gas Exchange (CO<sub>2</sub> Sequestration)

The latest research going on in the field of CO<sub>2</sub> sequestration for gas hydrates worldwide is explained as per follow:-

Chun-Gang et al. [11] in their study has explained hydrate based CO<sub>2</sub> separation and capture from gas mixture containing CO<sub>2</sub> is considered as one of the novel technology to reduce the anthropological release CO<sub>2</sub> into the atmosphere. The article has critically discussed the hydrate contain CO<sub>2</sub> formation equilibrium conditions, various hydrate promoters, molecular level measurement methods and various equipments for hydrate based CO<sub>2</sub> separation technologies. A novel computation model combining conventional model have been developed for more accurate prediction. Either kinetic additive or thermodynamic additive can solve all problems related to hydrate based CO<sub>2</sub> separation hence combination of additives have been developed.

Jiafei et al. [12] has discussed the exploitation of CH<sub>4</sub> from natural gas hydrates by CO<sub>2</sub>. It has given the latest information on the feasibility of replacement of CH<sub>4</sub> from natural gas hydrate CO<sub>2</sub> from kinetic and thermodynamic angle by experimental and simulation approach. The multistate simulation combined the phase field theory and molecular dynamic for analyzing the replacement microscopic mechanism. The factor influencing replacement reaction is mainly phase of CO<sub>2</sub>, initial temperature and pressure and additives. The efficiency of this replacement can be improved by further studying in this area

Igboanus [13] has discussed the global geographical distribution of gas hydrates and their occurrence. Particularly, it has explained the presence of hydrates on the Nigerian continental shelf. The various aspects of hydrate like hydrates as potential energy resource, climate change, ocean floor instability for large scale CO<sub>2</sub> sequestration has been discussed. The Nigerian hydrates are biogenic in origin. At present Nigeria has no national program for natural gas hydrates exploitation as other countries like USA, Japan, and India.

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SUN et al. [14] has discussed various hydrates based technologies. Hydrates are considered to separate components of gas mixtures like capturing greenhouse gases, capturing organic contaminants, capturing hydrogen from mixture of hydrogen and light hydrocarbon, capturing methane from coal bed, for separating ethane and methane. Comparable to conventional separating techniques this technique is more efficient. The only drawback of this technology is requirement of high pressure due to which it is not viable commercially. Additives are used to resolve this issue to some extent. They are considered for Methane gas storage, due to their high safety and storage capacity hydrates are commercially appealing. Drawbacks of this technique are: Rate of formation is slow, large amount water remains un-reacted, problems regarding reliability, economical aspect. Surfactant and additive are added to improve the hydrate formation rate.

Yanhong et al. [15] has discussed Hydrate based carbon dioxide capture (HBCC), technology used in separation of gas hydrates is one of the best methods for carbon dioxide capture and storage. In this process carbon dioxide is stored in solid form. Carbon dioxide requires lowest pressure at 270 K for combining with water cavities, hence it has highest affinity among above other gases. So, carbon dioxide can be captured through hydrate based technology. Carbon dioxide capture process based on hydrate technology involves two separate process for recovery and disposal. Carbon dioxide from flue gas, synthesis gas and biogas or natural gas can be separated using this technique. In recovery process these gases are fed to hydrate reactor which also gets water input, here water and carbon dioxide hydrate are formed and sent to decomposing reactor and remaining gases are sent for further processing. In decomposing section carbon dioxide is separated and recovered, water and slurry are recycled to hydrate reactor. In disposal process, gases containing carbon dioxide are fed to hydrate reactor where carbon dioxide hydrates are formed and like in recovery process remaining gases are sent for processing. Additives are used for moderating formation of carbon dioxide hydrate. Additives used are tetrabutyl ammonium salts of fluoride (TBAF), chloride (TBAC), bromide (TBAB) and other quaternary ammonium salts with low concentrations. Capturing process has problems related to pressure and kinetics which are to be taken into consideration and need to be studied further. Along with these, efficiency needs to be improved which depends on various factors including pressure-temperature, hydration rate of carbon dioxide, energy needed for process.

Wei et al. [16] has explained various separation techniques for separating carbon dioxide from mixture of gases. Being heaviest molecule of mixture, carbon dioxide can be separated by cryogenic distillation but it's a costly technique. Industrially absorption method is used for separating carbon dioxide. Various studies have been carried out to develop new techniques for pre-combustion and post-combustion capture of carbon dioxide which are based on adsorption, ammonia carbonation, absorption, distillation, hydrate formation, membrane diffusion etc. Feasibility of any technique depends upon its implementation cost commercially. Carbon dioxide capture through adsorption is a common thing. In this process emissions in gas phase are not generated. Various adsorbents like Amine-immobilized on MCM-41, SBA-15, Zeolite 13 X, Beta-zeolite, Amine modified activated carbon FeZSM-5 etc., are used. Problems related with adsorption processes are Carbon dioxide adsorption capacity (CAC) and pore volume is reduced due to amine impregnation which leads to plugging of supporting pores. These adsorbents have lower CAC than 13X zeolite. Nitrogen oxide adsorption which is irreversible occurs. Carbon dioxide can be captured by solid sorbents like regenerable sodium carbonate, lithium silicate etc. Besides these other techniques

like electrochemical pumps, electrically supported absorption and adsorption, by forming hydrates. The separation of CO<sub>2</sub> by CO<sub>2</sub> hydrate formation was revealed. The formation of hydrate for CO<sub>2</sub> capture seems very attractive but the requirement of high pressure for the formation of hydrates makes it less efficient [17].

Further research is needed in order to make novel technique like CO<sub>2</sub> sequestration of gas hydrate formation economic and commercial.

## Techniques for Exploitation of Gas From Natural Gas Hydrates Economically Viable and Environment Friendly

To make the gas hydrates exploitation economically viable and side by side making their exploitation environment friendly the CO<sub>2</sub> sequestration of gas hydrates seems an attractive and suitable option which have been studied in lab scale and as well as successfully carried out at field testing of gas hydrates by CO<sub>2</sub> Sequestration. Hydrate formation is an exothermic reaction. Actually by this technology the heat of dissociation of methane hydrate is provided by heat of formation of CO<sub>2</sub> gas hydrates because heat of formation of CO<sub>2</sub> gas hydrate exceeds the heat of dissociation of methane hydrates. In order to make this technology economically viable the intensive investigation is required which is going on. If we are able to make this technology successful then we can get tremendous amount of energy available by recuing the global warming. Global warming and energy are the burning issues of the century. This technology can give energy simultaneously by reducing global warming.

## Conclusion

An enormous amount of methane is available in the gas hydrates. They are present worldwide at the bottom of oceans and permafrost regions. Even a small percentage of which could meet the energy requirements of the world for centuries. If exploited properly, gas hydrates will be the next generation energy resource. CO<sub>2</sub> Sequestration is one such technology which can take energy from this resource and can reduce global warming side by side by sinking CO<sub>2</sub> in gas hydrates. This technology has been effective and successful at laboratory scale. Pilot scale production test have been completed in permafrost region and in marine gas hydrate deposit to test the possible gas recovery technology from hydrate bearing reservoir.

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