NATURAL GAS HYDRATES: THE FUTURE’S FUEL

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ABSTRACT
In recent years, the topics of naturally occurring gas hydrates have attracted major interest worldwide due to the fact that they may play a dominant role as possible energy resources in the future. Prior to this natural gas hydrates were mainly viewed at as a source of operational problems in gas processing and transportation equipment. The historical background and development of natural gas hydrates is reviewed as well as the necessary fundamental information about the structures of gas hydrates. One prerequisite of stable operation of gas processing plants as well as the allocation of gas deposit is the exact knowledge of the hydrate stability (equilibrium) data. Whereas a lot of data have already been measured and based on this reliable computation methods have been developed, there is still the necessity to measure equilibrium data to further improve the accuracy of the models.

Key Words: Global energy, Nuclear energy, Population, Hydroelectricity, Natural gas

INTRODUCTION

Energy, ‘the ability to do work’ utilizing the forces of nature or the composition of dead organic material, is essential for meeting basic human needs, extending life expectancy and providing an acceptable living standard. We have progressed over many thousands of years from a primitive life, which depended for energy on the food that could be gathered, to the hunters who had more food and used fire for heating and cooking, to the early farmers who used domesticated animals as a source of energy to do work. Then, we harnessed of wind and water power. Later, the industrial revolution, based on coal and providing steam power, laid the foundations for today’s technological society, with significant developments such as the internal combustion engine for transport and the large-scale generation of electricity (Fig. 1).

The global demand of energy is increasing with world population. The past century has been one of highest population and energy consumption growth. Over the past decade, the population on Earth grew from 6.065 billion in 2001 to approx. 7.0 billion in 2011, while the energy consumption grew from 9434.0 million Tons of Oil Equivalent (TOE) to 12274.6 million TOE¹.

Currently, the primary fuels being used are mainly oil, natural gas and coal which accounted for the consumption of 4095.1, 2905.6 and 3724.3 million tons of oil equivalents respectively.¹ Some amount of nuclear energy (599.3 million TOE) and hydroelectricity (791.5 million TOE) were also used worldwide in 2011. Since, the potential energy resources of uranium on Earth do not exceed 4.5% of resources from oil gas and coal, oil, gas and coal are the primary resources of fuel for future but they are limited.

DISCUSSION

Natural gas hydrates
Natural gas hydrates are solid crystalline, ice-like substances composed of water, methane and usually a small amount of other gases present in natural gas. The gases, mainly methane are trapped in cages of a hydrogen-bonded water framework. These natural gas hydrates are sometimes also called as Methane-ice (Fig. 2).

Methane hydrates is a naturally-occurring frozen compound formed when water and methane combine at moderate pressure and relatively low temperature conditions. Methane hydrates represent a highly concentrated form of methane, with a cubic meter of idealized methane hydrate...
containing 0.8 m$^3$ of water and more than 160 m$^3$ of methane at standard temperature-pressure conditions. Ethane, propane and carbon dioxide and similar gases can also form gas hydrates and individual molecules of these gases are often incorporated into gas hydrates that contain predominantly methane. Both on a global volumetric basis and in terms of areal distribution, methane hydrates are the most important type of natural gas hydrate.

**Fig. 1**: The role of different energy in the 20th Century, %

**Fig. 2**: Fire on ice

**Structure of natural gas hydrates (Clathrates)**

Clathrates are substances having a lattice-like structure or appearance in which molecules of one substance are completely enclosed within the crystal structure of another. The gas molecules (guests) are trapped in water cavities (hosts) that are composed of hydrogen bonded water molecules CH$_4$ (most common), CO$_2$, H$_2$S form hydrates (Fig. 3).

**Fig. 3**: Gas hydrate’s structure
Natural gas hydrates as a promising energy source
The huge demand of energy, which is increasing day by day, can be fulfilled globally if we develop some technology to recover the large deposits of Natural Gas Hydrates. Natural gas hydrates are a vast potential, though not presently commercial, source of additional natural gas. One of the most appealing aspects of this potential new gas source is that large deposits are located near the expected demand growth areas. Large volumes of natural gas hydrates are known to exist in a relatively concentrated form at numerous locations. Current estimates indicate that the mass of carbon trapped in natural gas hydrates is more than half of the world’s total organic carbon and twice the amount of carbon to be found in all known fossil fuels (coal, oil and natural gas) on Earth. It is estimated that the global hydrate bound methane is 1.8-2.1*10^{16} m^{3} (Fig. 4)

![Fig. 4: World energy balance](image)

Gas hydrate deposits
The most promising regions to look for commercial deposits of gas-hydrate are the deepwater shelves, continental slopes and continental abyssal trenches, with water depths from 700 m to 2500 m. However, the most promising resources of gas-hydrates are concentrated in only 9% to 12% of the ocean floor. Rock formations with pressures and temperatures favorable for the formation of gas-hydrates are abundant. However, in most of the rock, the saturation of gas hydrate will be too low to be commercially developed. For example, on Messoyakha only 40 m of hydrate has been identified in the HFZ layers that are 600 m thick. This corresponds to 6.6% of the thickness of the HFZ. In the Nankai Trough offshore Japan, thermodynamic conditions corresponding to formation and stable existence GHD appear in 505 m of overall thickness of the sedimentary rocks. However, only 17 m contains gashydrates at reasonable saturations, which is only 3.4% of the total thickness.

At Blake Ridge, located on the east coast of the USA, the hydrate formation zone is 440 m thick. However, only 7.5 m, which composes only 1.7% of the thickness of the HFZ, contains hydrate.

Availability of gas hydrates
The mechanism of how gas-hydrate deposits are formed and where hydrates are located has been affected by numerous factors, such as:
(1) Thermodynamic regime in the region
(2) Intensity of generation and migration of hydrocarbons
(3) Composition of the gas
(4) Degree of gas saturation and salinity of the reservoir water
(5) Structure of the porous medium  
(6) Lithologic characteristics of the section  
(7) Geothermal gradients in the zone of hydrate formation and in the basement rocks and  
(8) Phase state of hydrate formers

The hydrate formation zone (HFZ) represents the thickness of sediments in which the pressure and the temperature correspond to the thermodynamic conditions of stable existence of gas-hydrates of a specified composition (Fig. 5).

These HFZs are found where the Earth is cool, such as the Arctic and deep water. With an increase in the salinity of water, the thickness of the HFZ decreases. The thickness and the temperature of the HFZ in the offshore strongly depend on the value of sea bottom temperatures and gradient in the sediments. With an increase in sea bottom temperatures, the size of the HFZ decreases. In the regions where permafrost exists, the thickness of sediment in which gas-hydrate deposits exist can reach 400 to 800 m. The HFZ in the ocean is found in the deepwater shelf and the oceanic slope in depths of water 200 m or deeper for the conditions of in polar oceans and from 500 to 700 m or deeper for the equatorial regions. The upper boundary of the HFZ offshore is located near the sea floor.

Magnitude and global distribution of the hydrate resource

Knowledge of the occurrence of in situ gas hydrates is very incomplete and is obtained from both indirect and direct evidence. There have been 23 locations where irrefutable evidence of hydrates has been seen through direct recovery of hydrate samples: 3 in the permafrost and 20 in ocean environments. In permafrost regions, evidence of gas hydrate is provided two ongoing R&D programs (discussed below) and by analysis of industry 3-D seismic data and data obtained during the drilling and logging conventional oil and gas wells. The ability to prospect for gas hydrate deposits using this data has recently been demonstrated in the Prudhoe Bay region of the Alaska North Slope. In the marine environment, the bulk of the data supporting the interpretation of gas hydrates at the majority of locations in indirect indicators (such as Bottom simulating reflections) on relatively low-quality 2-D seismic data. However, direct gas hydrate detection and characterization from marine 3-D data has recently been shown by Dai et al. and the use of 4-component ocean bottom seismic also shows great promise (Fig. 6).
Given the relative abundance of marine gas hydrate resources, these occurrences will likely be the primary targets for future R&D activities. However, given the favorable economics of conducting long-term field programs in the Arctic (as opposed to the deep water, it is expected that arctic R&D activities will also continue. Two countries, the U.S., and Japan are making considerable R&D investments in the Arctic, under the reasoning that the information gained on the behaviour of gas hydrate bearing sand reservoirs can be readily transferred to the study of marine resources at a later date.

Estimates of gas trapped in hydrates and related uncertainties

These estimates range from the maximum values of Trofimuk et al., (3.053x10^{18} \text{ m}^3 \text{ STP} of CH_4), based on the assumption that hydrates could occur wherever a satisfactory P-T regime exists, to the minimum values of Soloviev (2x10^{14} \text{ m}^3 \text{ STP}, accounting for limiting factors such as CH_4 availability, limited organic matter, porosity \(\phi\), the thermal history of various regions, etc.). All the estimates involve extrapolation of a limited amount of fairly well known, localized geological data to a global level. The Klauda and Sandler estimate is based on a state-of-the-art model that involves:

1. A new \textit{ab initio} thermodynamic model that includes the effects of pores and salt,
2. Estimates of the locus of the intersection of the geothermal gradient with the phase boundary (obtained from measured local temperatures and gradients in the world oceans) and
3. Measured local organic sediment contents that served as inputs to the methanogenesis mass transfer model of Davie and Buffett.

The model enables prediction of most recorded occurrences of hydrates and reasonable explanations for the remaining exceptions. The large amount of hydrates predicted by Klauda and Sandler includes both very deep hydrates and much dispersed hydrates, many of which are not accounted for by the other models or are not discovered by sampling due to dissociation. When only continental hydrates are considered, Klauda and Sandler predict 4.4x10^{16} \text{ m}^3 (\text{ STP}) of gas in hydrates. None of the estimates of natural gas hydrates are well defined and therefore they are all speculative to a certain extent.

However, even the most conservative estimates suggest enormous amounts of gas in hydrated form, the magnitude of which can be appreciated by comparing them to the current rate of 10^{12} \text{ m}^3 \text{ STP} of gas-equivalent annual energy consumption in the United States.
estimates are comparatively large relative to estimates of the conventional gas reserve of 1.5x10^{14} \text{ m}^3 of methane indicated that his estimate of 1.8x10^{16} \text{ m}^3 of methane in hydrates may surpass the available, recoverable conventional CH$_4$ by two orders of magnitude, or a factor of two larger than the CH$_4$-equivalent of the total of all fossil fuel deposits.

The only systematic assessment U.S. hydrate resources to date have been by Collett. He Recovery techniques

It is widely agreed that existing technology can be used to produce gas hydrates. The production methods being evaluated now have changed little since the early 1980s, when Holder et al., discussed the technical merit and economic feasibility of thermal stimulation, depressurization and chemical inhibition for the production of gas from hydrates. This section reviews production methods, discusses some production scenarios and briefly mentions potential hazards associated with gas production from methane hydrates.

Short-term production tests at the permafrost Mallik and Mt. Elbert wells and laboratory simulations on sediment cores have produced important data on gas production via depressurization and/or thermal stimulation. Here we consider each of the primary production methods in turn.

Thermal stimulation

Refers to warming the formation through the injection of heated fluid or potentially direct heating of the formation, as shown schematically in Fig. 7. Thermal stimulation is energy intensive and will lead to relatively slow, conduction limited dissociation of gas hydrates unless warmer pore fluids become mobilized and increase the volume of the formation exposed to higher temperatures. The endothermic nature of gas hydrate dissociation also presents a challenge to thermal stimulation the cooling associated with dissociation (and in some cases, gas expansion) will partially offset artificial warming of the formation, meaning that more heat must be introduced to drive continued dissociation and prevent formation of new gas hydrate. In terrestrial settings thermal stimulation must be carefully controlled to assigned probabilities to 12 different factors (geological attributes correlated with the existence of hydrates) to estimate the 50% probability (mean) estimate of hydrate resources within the United States at 9x10^{15} \text{ m}^3 of CH$_4$ (with the 95% probability estimate at 3x10^{15} \text{ m}^3 and the 5% probability estimate at 1.9x10^{16} \text{ m}^3), i.e., the mean hydrate value indicates 300 times more hydrated gas than the gas in the total remaining recoverable conventional resources.

Depressurization

Shown schematically in Fig. 7, has emerged as the preferred and more economical means of producing gas from methane hydrates during most of a well’s life. Depressurization does not require large energy expenditure and can be used to drive dissociation of a significant volume of gas hydrate relatively rapidly.

Chemical inhibition

Exploits the fact that gas hydrate stability is inhibited in the presence of certain organic (e.g., glycol) or ionic (seawater or brine) compounds. Seawater or other inhibitors might be needed during some stages of production of gas from methane hydrate deposits, but would not be the primary means of dissociating gas hydrate nor used for an extended period or on a large scale.

Production challenges

Peak production for conventional gas usually occurs soon after a well is established. In contrast, reaching peak production of gas from gas hydrate deposits alone (i.e., those not associated with free gas) may take several years, largely due to the time required for a dissociation front to propagate through the hydrate-bearing sediments. As noted above, both the rapid expansion of gas and the endothermic heat of hydrate dissociation might cool sediments and lead to the formation of secondary gas hydrate or ice, a notion challenged by recent results of Anderson et al. If such cooling processes occur and are not properly controlled, they have the potential to dramatically reduce net production and production rates. In practice, the anticipated reduced production from a gas hydrate well
Production from methane hydrate deposits does pose special challenges for commercialization. For example, hydrate dissociation frees significant volumes of free water and the study by Walsh et al. shows nearly 2500 bbl of water produced for every million cubic feet of gas produced from deepwater methane hydrate early in the development of a hypothetical deepwater reservoir. This figure drops to ~100-200 bbl water produced per million cubic feet of gas produced during much of the life of the well before climbing rapidly after more than a decade into the hypothetical production scenario.

Another issue that distinguishes gas hydrate production from production of conventional gas is that gas hydrate reservoirs occur at significantly lower pressure than conventional gas reservoirs. This means less pressure is available to drive gas flow into the production well and more energy will likely need to be expended to lift gas from the formation. On the other hand, the lower pressure of the formation means that there is less potential for gas...
expansion or uncontrolled flow of gas during production, somewhat lowering the risk of a catastrophic event.\textsuperscript{10,11}

\textbf{Hazards}

There have sometimes been concerns that the production of gas from gas hydrate is inherently risky and could pose unique or unknown dangers for infrastructure or personnel\textsuperscript{12,13}, beyond those associated with conventional hydrocarbon production. It is possible that destabilization of natural hydrates (as opposed to those that form in pipelines and conduits) has occasionally affected the integrity of the seafloor or boreholes, led to well control problems or contributed to shallow water flows\textsuperscript{14,15}, but there is scant published evidence. The long-time industry practice of simply avoiding areas with known gas hydrates during production activities that target deeper, conventional hydrocarbons has become increasingly impractical with the push for more deepwater operations. The issue of risk related to drilling through gas hydrates, no less production of gas from methane hydrates, must therefore be directly addressed.

The first stage of the DOE/Chevron JIP drilling in the northern Gulf of Mexico was partially designed to determine whether drilling of low saturation gas hydrates, like those commonly encountered in the shallow subseafloor for deepwater environments, posed a manageable risk to drilling activities and borehole/seafloor stability.\textsuperscript{16,17} More than ten major deepwater drilling expeditions have now successfully targeted gas hydrates and experienced no major safety issues. Borehole stability modeling, careful drilling fluid management (i.e., temperature, weight of drilling mud) and planning for possible formation overpressures are critical for ensuring safe operations in gas hydrate wells, as in normal wells.\textsuperscript{18,19} Reservoir simulations for production of gas from even the highest saturation hydrate deposits have repeatedly shown that runaway dissociation, rapid gas migration and even blowouts are not typically concerns for gas hydrate wells.\textsuperscript{20-22} In fact, gas production from methane hydrate is always predicted to occur at a rate lower than the peak rate from a comparable conventional well and the key challenge in production from gas hydrates is ensuring that dissociation continues even while the endothermic heat of dissociation and other processes cool the formation. Reservoir simulation for gas hydrates does not yet accurately incorporate advanced geomechanics concepts.\textsuperscript{23-25} Thus, one risk factor that remains to be assessed is the potential for gas migrating away from a dissociating, high saturation gas hydrate deposit to find an existing fracture or to cause a new fracture to form in an overlying, relatively impermeable layer. Such a scenario might lead to unintended leakage of methane into other sediments or even emission of methane at the surface.

\textbf{CONCLUSION}

Natural gas hydrates are a promising source of future energy. It is the clean and eco friendly source of fuel. It is present in bulk amount and a large amount of reserves are yet to be explored. Research is going on of exploiting the natural gas hydrates reserves worldwide and to extract natural gas from them efficiently and profitably. Various methods have been employed till date for natural gas hydrate’s recovery which has been discussed in this report. Although economy is another milestone which is yet to be achieved for the commercialization of the processes. According to the researchers, it will take another decade for the commercialization of the process.

\textbf{REFERENCES}