Rapid Hydrate Formation, A Process for Transport and Storage of Natural Gas

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Introduction

Nearly 50 percent of worldwide natural gas reserves of ~6,609 trillion ft^3 (tcf) is considered stranded gas. Within the United States, 36 percent or ~86 tcf of the U.S natural gas reserves, totaling ~238 tcf, is classified as stranded gas [1-3]. The U.S. Geological Survey has also estimated that almost 1,700 tcf of new natural gas resources exist within the Arctic Circle [4]. While there is a current and future need for these energy sources, a need also exists for newer and more economic methods to store and transport this natural gas to markets. Facilities to compress the natural gas (CNG) or to liquefy it (LNG) also require large capital investment. Once the gas is in a transportable-state, it needs to be moved to market. The construction of new pipelines and/or railway systems is expensive and labor intensive. A possible solution to these problems would be a method of rapidly transforming the natural gas into gas hydrates. Mitsui Engineering and Ship Building (MES) has determined that methane hydrate could be stored and transported safely at about 253K under atmospheric pressure due to so called "self-preservation effect" [5]. MES also reports that a cost savings of between 18-25% for the production, transportation (1500-3500 nm), and regasification of natural gas hydrate as compared to LNG [5].

Gas hydrates are a unique class of chemical compounds where molecules of one compound (the guest material, methane) are enclosed, without bonding chemically, within an open solid lattice another compound (the host material, water) (see Figure 1). These types of compounds are known as clathrates. The guest molecules, usually gases, are of an appropriate size such that they fit within the cage formed by the host material. Common examples of gas hydrates are carbon dioxide/water and methane/water clathrates. At standard pressure and temperature, methane hydrate contains 164 volumes of methane for each volume of hydrate. The rate of formation for natural gas hydrate is slow and is one of the critical aspects that could hinder the industrial application of gas hydrate storage and transportation.

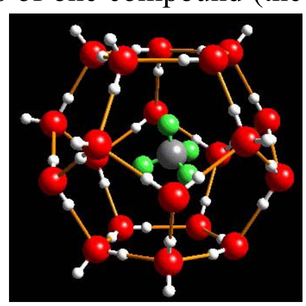

Figure 1. Model of Methane Hydrate

Results

Experimental results from our laboratories at the National Energy Technology Laboratory (NETL) show that rapid and continuous formation of methane hydrate, as well as other gas-derived hydrates is achievable. The goal of this technology is to provide a safer, environmentally friendly, and potentially lower-cost alternative for natural gas storage and transportation. In the laboratory, methane hydrate formation typically takes anywhere from 6 hours to several days or weeks. However, NETL's rapid hydrate formation process allows instantaneous and continuous methane hydrate formation by use of a novel nozzle resulting in a continuous process producing hydrates at lower capitol and energy costs. Traditionally, synthetic methane hydrates are formed by mixing of water and methane in a sealed pressure vessel at elevated pressures and reduced temperatures. Under the proper conditions, the mixture will form a hydrate after several hours. Our novel patent-pending technology produces gas hydrates from a mixture of water and a hydrate-forming gas instantaneously. The two-phase mixture is created in a mixing zone contained within the body of the spray nozzle. The mixture is then sprayed into a reaction vessel under pressure and temperature conditions suitable for gas hydrate formation. The nozzle allows for improved gas solubility and heat transfer. The result is the instantaneous and continuous formation of gas hydrates with a greatly reduced induction time for gas hydrate crystal formation. Figure 2 shows the rapid formation of the methane hydrate as it exits the injection nozzle. In order to confirm that methane hydrate was being formed (as opposed to water ice); a sample was collected and analyzed using Raman spectroscopy. The resulting spectrum exhibited the two signature peaks of methane hydrate, 2904 cm^{-1} and 2014 cm^{-1}, confirming the formation of methane hydrate.

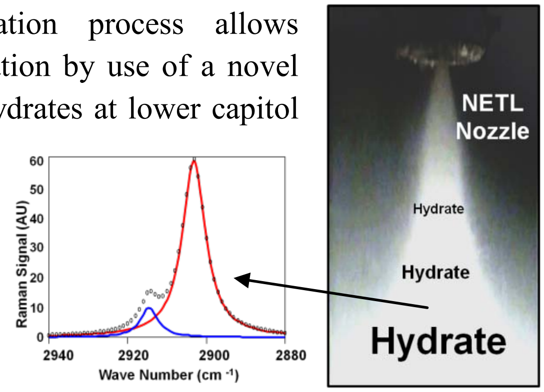

Figure 2. Methane Hydrate Rapid Formation At Nozzle And Raman Spectrum Confirming Formation Of Methane Hydrate

This technology may also be applicable to carbon dioxide sequestration, separation of mixed gases, cold energy storage, transportation fuels, and desalination processes. Many gases form hydrates, such as methane, carbon dioxide, hydrogen sulfide, ethane, etc. (These gases are common components of natural gas). Each gas will form at a pressure and temperature that is different from other gases present (see Figure 3). By selecting the proper pressure and temperature, gas mixtures can be used as a feed for the rapid formation nozzle where an individual gas will be formed as a hydrate, leaving all the other gases in the gas phase. By repeating the process on the left over gas at a different pressure and temperature, a different gas can be separated from the mixture via hydrate formation, and so on. Another use for the rapid hydrate formation technology is in the separation of individual gas components from natural gas mixtures. An example where this technology can be applied is with natural gas. Natural gas is a mixture of several gases such as methane, ethane, propane, butane, carbon dioxide, hydrogen sulfide, etc. The concentrations of these gases vary by location. Several of these gases are not desirable for combustion, while others, if

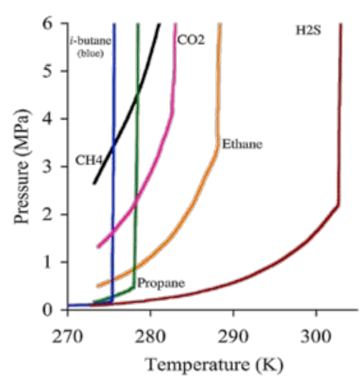

Figure 3. Gas Hydrate Formation Curves [16]

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present in high enough concentrations, are more valuable commercially than the mixture if they could be economically separated. Selective removal of these gases using rapid hydrate formation could be the answer. This is important for the gas being recovered from the Marcellus shale. The gas contained in the Marcellus shale can contain over 16% ethane. [17] This results in a natural gas that has a BTU value much higher than the 1000 BTU/FT^3. Normally a high BTU gas would be blended with a lower BTU gas, however, the Marcellus region does not have the gas blending luxury because there is little infrastructure in place. It has been estimated that within the next few years, unless an ecconomical method of separating the ethane from the rest of the gases in the Marcellus shale gas, that the full production potential of the wells will not be able to be used. Separating the ethane from this gas by selective rapid hydrate formation could solve this problem and generate a high-value product, ethane (ethane typically sells for roughly twice the value of natural gas). Not only would this technology separate the ethane from the Marcellus shale gas, but keeping it as a hydrate would facilitate its transportation to the end user.

Methane hydrate can be stored as a solid or semi-solid material at atmospheric pressure and temperatures between -10 and -20° Celsius—the same temperature range used to transport frozen foods in trucks, box cars, and ships [6-11]. Because no new transportation technology is required (see Figure 4), methane hydrate has the potential to provide a tremendous cost savings over the transport of compressed and liquefied natural gas [12-15]. Reduced capital and operational costs for small to mid-sized gas fields make the adoption of gas hydrate technology attractive to commercial interests when compared to construction and operation of a liquefied natural gas (LNG) facility or construction of pipelines. Additional advantages of hydrate storage and transport over LNG are: hydrate formation and transport can be used for all gas fields, not the 2% of fields suitable for LNG (including "stranded" gas fields and associated gas); up to a 24% reduction in capital investment compared to LNG [12,15], up to a 30% reduction in transportation energy compared to LNG, ships are able to dock at any port and transport the hydrate using existing infrastructure [12,15]; high-pressure storage is not necessary, cryogenic storage temperatures are not necessary, large amounts of "cold heat" is produced upon dissociation of the hydrate, pure water is produced as byproduct of dissociation; and increase in the safety of handling the product.

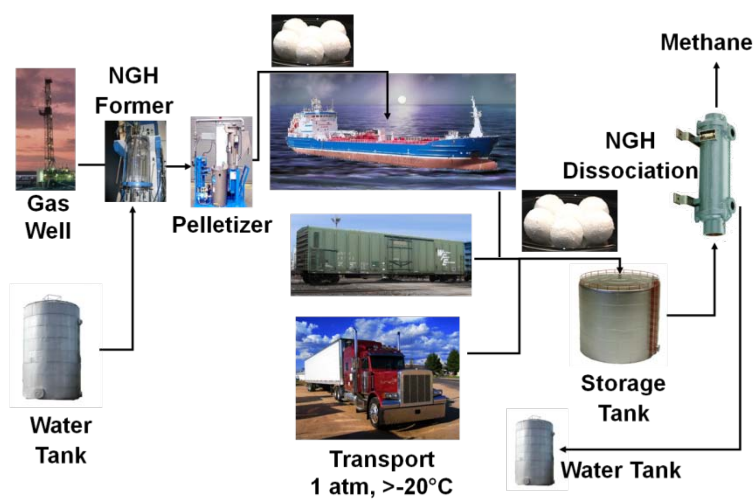

Figure 4. Schematic For The Transport Of Natural Gas Via Hydrates

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