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HYDRATE TECHNOLOGY FOR TRANSPORTING NATURAL GAS

R A Dawe+, S Thomas and M Kromah
Petroleum Engineering Unit
Department of Chemical Engineering
The University of West Indies
Trinidad
+ Email: radawe@eng.uwi.tt

ABSTRACT

Natural gas hydrate (NGH) is a viable alternative to LNG (Liquefied Natural Gas) or pipelines for the transportation of natural gas from source to demand. It involves three stages: production, transportation and re-gasification. The production of the hydrate occurs at pressures >50 bar at temperatures ~10°C in the presence of water and natural gas (particularly methane, ethane, propane). Transportation is by insulated bulk carrier at around –5 °C and atmospheric pressure or 0 °C at 10 bar, and re-gasification is carried out with controlled heating using water. The hydrate yields ~150 sm³ of natural gas per cubic metre of hydrate. The transportation of natural gas by hydrate should have significant lower capital and operating costs for the movement of quantities of natural gas over adverse conditions compared to pipeline or LNG. The simplicity and flexibility of the process make the natural gas concept worth the development required.

Key words: Hydrates, Natural gas, Natural gas transport**.**

Units: The petroleum industry uses a variety of units and conversion from one unit to another is often necessary. The major conversions for this paper are: -
$1m^3 \equiv 6.29$ bbl (barrels) $\equiv 35.3$ scf. 1bbl = 5.615 cf. 1metric tonne oil ~ 7.5 bbl.
Standard conditions represented as scf and sm^3 are 60°F and 14.7 psi and 15 °C and 1 bar.
Gas volumes are given as M = thousand (10^3); MM = million (10^6); B = billion (10^9); T = trillion (10^{12}) scf. 1,000 MM scf = 1 B scf = 28.3 MM sm^3.
1 MM scf/day = 10 MM sm^3/year ≅ 7,500 metric tonnes LNG / year.
6000 scf gas contains approximately the same energy as 1 bbl oil. Thus if gas costs \$1.00 /Mscf the oil energy equivalent is \$6.00/bbl and at \$2.50 /Mscf the oil energy equivalent is \$15.00 /bbl.
100scf of gas ≅1 therm ≅100,000 BTU. 1 kilowatt-hour =10^3 watt-hour = 3,412 BTU
1 MM scf gas /day can supply ~10 megawatt electricity generating capacity continuously running.

I. INTRODUCTION

For decades getting gas to market has been problematical and prevented the development of many fields. The North Field in Qatar is a good example. It was discovered in 1971, but LNG export only started in 1997[1,2]. Current transport methods are pipelines and liquefied natural gas (LNG) [3]. Other potential methods of getting gas, its energy or its products to market to monetise it include compressed natural gas (CNG), gas to solids (GtS, i.e. gas hydrates), power generation (gas to wire, GtW i.e. generate electricity at the wellsite and transport the electricity by cable), gas molecules to liquids (GtL, for example methanol, ammonia, clean liquid fuel, plastics precursors) and gas energy to products, (such as manufacture of cement, iron and steel and aluminium) [1-5]. Natural Gas Hydrate technology is a possible way forward, GtS, and is discussed in this paper.

II. GAS SOURCES

Gas may be associated gas, which is gas produced along with oil as pressure drops, or non-associated gas from reservoirs with only gas within the reservoir [5]. Gas is stranded if it has no current market, e.g. the many on- or offshore fields where there is no pipeline, or for fields where there is flaring prohibition of associated gas. Worldwide, governments are mandatory stopping flaring of associated gas as the public perceives that it is a waste of a valuable non-renewable resource. When such restrictions occur the gas must somehow be exported or reinjected, otherwise oil production must stop. Finding new ways to export the gas to market at rates cheaper than LNG has many attractions.

III. NATURAL GAS HYDRATE

Mostly in the industry, natural gas hydrates are a pipeline nuisance and safety hazard, and require considerable vigilance by the operators to ensure that they do not form [7]. Hydrates can block pipelines if precautions, such as methanol injection, are not taken. On the other hand, vast quantities of gas hydrate have been found in permafrost and at the seabed in depths below 500 m (1500 ft). Estimates of the volume of methane in these hydrates is 2 or perhaps as high as 10000 times as much as current conventional gas reserves, leading to worldwide interest in finding methods to extract the gas safely [8-11]. However natural gas hydrate slurry can be deliberately formed by mixing natural gas and water at 80-100 bar and 2-10 ^{o}C. One process group has described the process simply as, 'just add water and stir' [6]. It has been found that if this slurry is refrigerated to below –10 ^{o}C, it decomposes very slowly at atmospheric pressure, so that the hydrate could be transported by ship to market in simple insulated (inexpensive compared to LNG carriers) bulk carriers i.e. in a large 'thermos flask' at near adiabatic conditions.

Hydrate is the product of mixing natural gas with liquid water to form a stable snow-like substance. It is created when certain small molecules, particularly methane ethane and propane, stabilise the hydrogen bonds within water to form a 3-dimensional cage like structure with the gas molecules trapped within the cages [6-12], figure 1. The thermodynamic and phase diagrams of water, hydrate with various gases have all been well researched and documented [6-11]. For hydrates to form the conditions have to be in the high pressure /low temperature side of the equilibrium curve of the phase diagram with the appropriate hydrate forming gas and liquid water. The heat of formation is 410 kJ/kg i.e. exothermic so heat must be removed to maintain constant temperature conditions in the reactor. In theory, hydrate can absorb 180 sm^3 of gas if all the sites are used, but so far only about 160sm^3 have been recovered from 1m^3 of hydrate. This is because natural hydrate is non-stoichiometric so has variation in its composition. The method of formation, gas composition, pressure and temperature all contribute to the 'degree of filling'. Hydrate has a density of around 950 kg/m^3 and contains about 0.85 m^3/m^3 of water, so will float on liquid water.

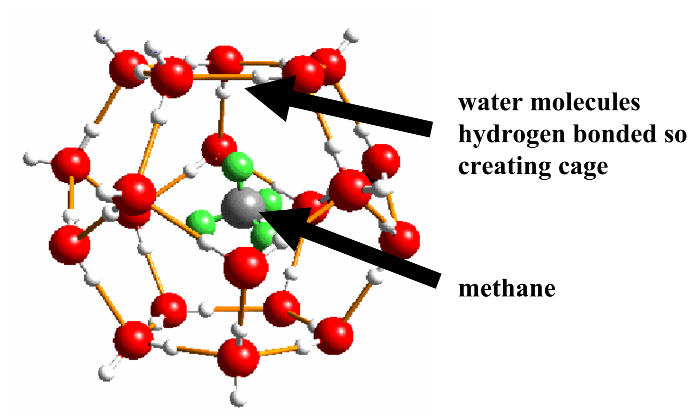


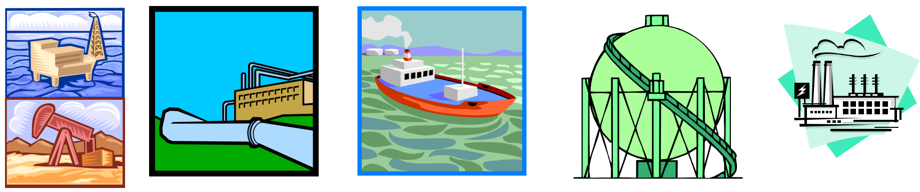
Fig. (1)

A hydrate cage is made up of several water molecules held together by hydrogen bonds. These types of structures, known as clathrates, have been well studied but are complex. Water has 3 different cages within its lattice which can hold different sized molecules; sI containing 46 water molecules per 8 gas molecules, figure 1, sII containing 136 water molecules per 24 gas molecules and sH containing 34 water molecules per 6 gas molecules. The main natural gas hydrate formers are methane and ethane into sI, and propane and isobutane into sII. Structure sH has only recently been fully identified and is a larger cage and can accommodate larger molecules including benzene but a mixture of gases are needed, particularly methane, to make the structure stable thermodynamically [9].

Hydrate is therefore very effective for gas storage as 1 m^3 of hydrate will contain about 160 sm^3 gas (5,600 scf) and 0.85 m^3 water. The advantage of storing gas in the hydrate state is that high volumes of gas are stored in the hydrate state which is especially efficient at relatively low pressures, as 160 volumes of gas per unit volume can be stored at normal temperatures (0 to -5 ^{o}C) compared to the 200 sm^3 compressed at high pressure at >200bar as CNG, or the 643 sm^3 liquid LNG but at -161 ^{o}C.

IV. THE HYDRATE TRANSPORT PROCESS

There are a number of stages to consider in transporting gas from the field to the electricity generator. The total process involves the manufacture of natural gas hydrates from natural gas and water, the transportation of the hydrate by ship and the re-gasification of the hydrate to natural gas and water, figure 2.



field manufacture transport storage & regassification electricity generation

Fig. (2) The hydrate chain

- gas production from field and transport to hydrate facility. The reservoir gas, whether associated or non-associated, would be produced to surface from the reservoir by normal petroleum engineering practice [5] and the transport of the gas to the hydrate manufacturing facility would be by pipeline.
- hydrate facility (temperature: ~10 ^{o}C and pressure 50-90 bar) located on-land, platform or floater. The manufacture of the hydrate could be carried out using mobile equipment for onshore and ship for offshore with minimal gas processing prior to hydrate formation, which is attractive commercially. Clearly for offshore stranded gas, the hydrate facility will have to be on a floating platform (FPSO – floating production, storage and offloading vessel) within the field or at some more sheltered place, depending on the water depth. The natural gas and water would be combined at pressure (50-90 bar) and temperature (5-15 ^{o}C) chosen from considerations of the equilibrium curve for the system [9]. The reactor temperature would be a few degrees below the equilibrium temperature to increase the reaction rate for the formation of natural gas hydrate. The hydrate manufacturing routine would have been designed and tested via pilot and test facilities [e.g. 6]. Typically the process would consist of, fig 3: -
    - gas in, cool and compress to about 10^{o}C and 50-90 bar (pressure depending on temperature and phase diagram)
    - combine with cooled water which is then pressured to 50 –90 bar
    - react in a series of tank reactors, keeping the process at constant temperature by cooling.
- after formation, excess gas and water would be separated from the hydrate and recycled. The hydrate is cooled, depressurised, compacted to make more stable and is then available to be transported.
- transport by insulated bulk carrier. The hydrate can be loaded onto moderately insulated ships via conveyers.
- at the market, discharge from carrier then regassification, where the slurry is melted back to gas and water by controlled warming for use in electricity power generation stations or other requirements, [12-16].

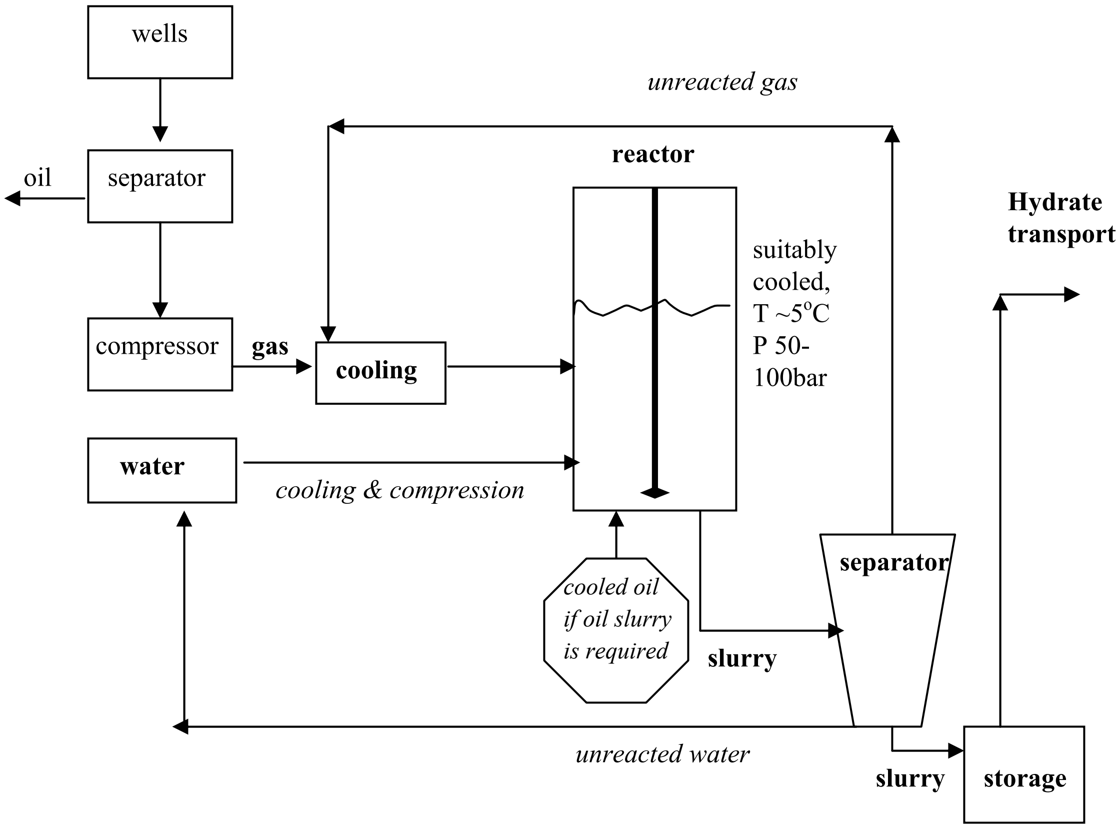


Fig. (3) hydrate production process

V. DESIGN CONSIDERATIONS

Various processes have been proposed and tested in the laboratory, with the variations being a hydrate consisting of a dry powder or a water- or an oil-based slurry, as discussed below. The selection and specification of equipment to separate the dilute slurry and remove the free, unconverted, water depends on the extent of water removal required and method of moving the hydrate to the transporter. For instance, to produce a dry solid (the 'dry' process) containing some 150 volumes of gas per volume of hydrate, virtually all of the free water needs to be removed.

The reactors operate at 5-10 ^{o}C and 50 – 90 bar, the exact conditions depending on the hydrate phase diagram. The cooling fluid may be any available and economical coolant and may be cold gas, cold water or a fluid from a neighbouring plant that needs to be heated. The output, perhaps 10 wt% hydrate from the reactor, can be pumped at 50 bar to a second and then perhaps to a third reactor where further fresh gas and water is added to the hydrate to continue the hydrate growth. The product from this reactor would contain >30 wt% hydrate plus unreacted water and gas.

Reactor cooling; as the hydrate creation process is exothermic, energy is released (410kJ/kg). This generated heat has to be removed from the system, which can be achieved in the reactor via a jacket through which a cooling fluid flows, keeping the reactor at constant temperature.

Separation: the hydrate manufacturing process produces a dry powder or a water- or oil-based slurry but further processing is needed before the finished hydrate product can be shipped [6]. The product could be sent to a separator, which could be a cyclone, screens or a centrifuge to separate the unreacted water and gas from the hydrate. The unreacted water and gas from the separator is recycled to the first reactor after recompression to 50 bar and cooling to 10 ^{o}C. The hydrate product from the separator may contain 90 wt% hydrate and 10 wt% free water.

Dry hydrate: this can be formed in two stages of water removal: a primary stage to achieve bulk separation, followed by a secondary stage to complete the dewatering. Then the dry hydrate is cooled to $-10^{o}C$ through a heat exchanger, which allows any remaining free water to solidify around the hydrate particles; this ice shield makes the hydrate less susceptible to melting. This step improves the stability of the hydrate and also increases the hydrate particle size from 1-10mm to 5-15mm. This dry hydrate is fully stable at atmospheric pressure at around -40 ^{o}C, the exact temperature depending on the composition of hydrate. This has been successfully demonstrated in laboratory testing at kg scale, [6].

Water-based slurry: alternatively, a partial dewatering can be carried out to produce a concentrated, but pumpable, hydrate slurry ('slurry' process) containing around 75 volumes of gas per volume of hydrate, but water freezing out as ice can be problematical. Dewatering techniques are still being developed [6].

Oil-based slurry: the mixing of hydrate with refrigerated hydrocarbon liquids (e.g. light crude oil) for easy pumpability at ~-10^{o}C has been proposed to enable the hydrate to transfer from the generator to storage or transporter [14-16]. Clearly additional processing to remove the oil (hydrate contaminant) at the delivery stage would be required but pumpability may be less problematical. In addition, the hydrocarbon liquid requires increased refrigeration to maintain hydrate stability and this is additional (energy) cost at each of the manufacturing, transport and regassification stages.

Storage: hydrate has been stored in the laboratory at $-5^{o}C$ and atmospheric pressure for periods of several months, with minimal loss of gas.

Transporter: the best means of transporting the hydrate to the customer is by insulated bulk carriers. Such bulk carriers normally have 100mm of insulation and therefore do not need to be refrigerated as the ‘cold’ within the hydrate and the adiabatic conditions are sufficient. The hydrate will be loaded onto the ship via a covered mass conveyer or pumped as a slurry, whether water- or oil-based. The holds of the carriers would receive the hydrate.

Loading, unloading and freezing: the main difficulty with the use of the bulk carrier is the unloading process, as any free water may freeze and create large lumps of hydrate which would cause blockages in the conveying system. Laboratory experiments have shown that it is difficult to remove the dry hydrate (possibly 90 wt% hydrate and 10 wt% water as a shield) or the slurry from the vessel, without adding some fluid (natural gas or water) so that it can be de-iced before being pumped. The principal advantage of a dry solid hydrate is that it can be stored and transported at sub-zero temperatures by, conveyer and shipped at atmospheric pressure. For the concentrated hydrate slurry alternate laboratory experiments suggest that it would need pressure containers at around 10 bar and 2 ^{o}C on a vessel similar to a LPG ship, which is extra cost. Alternatively, but less effective could be the storing of the product in large plastic containers which are then lifted by crane into the carrier’s hold. On arrival, the customer transports the hydrate to the plant where the plastic containers can be emptied into the storage tanks for melting.

Re-gasification; the re-gasification process is a simple addition of heat to provide the energy of dissociation of the hydrate (410 kJ/kg). The hydrate enters the plant at temperatures below 0 ^{o}C and is pumped into a storage vessel where warm water is added, probably as a spray, to the hydrate to supply the heat to melt the hydrate to natural gas and water. The natural gas is compressed and dried in an ethylene glycol absorption unit (or some other appropriate solvent with an affinity for water but not for the components of natural gas). The gas is collected and is available for power generation. It may need to be recompressed to the design pressure of the power generator.

The water melted from the hydrate and water used in the melting process would be collected from the bottom of the vessel and now is at around 5 ^{o}C and can be used as a cooling fluid for perhaps cold storage or air conditioning. As the re-gasification plant is probably located near to the power generation plant, the water for the melting of the hydrate may be warmed using waste heat from the power generation plant.

Further pilot studies would be needed when a specific project has been identified.

VI. DISCUSSION AND CONCLUSIONS

Any alternative technology for handling and disposal of associated gas for fields where pipelines or gas re-injection are not options must show commercial benefits and competitive advantage. The competitive advantage of the GtS process over other non-pipeline gas technologies is that it is intrinsically a simpler processes and, as a concept, far easier to implement and feasible at lower capital costs. The processes do not involve extreme temperature, either high or low, do not require an oxidant or a catalyst, nor feature any complex unit operations other than standard process equipment. In addition, the technology is able to cope with an intermittent and variable profile of gas production with time, as is usually the case with associated gas. The major parts of the hydrate manufacturing process have been tested up to pilot plant level, [6].

Analysts [16-18] claim that transportation of natural gas as hydrate is feasible at costs believed to be less than for LNG, which for Qatar is around $15 bbl oil equivalent ($2.5 Mscf) [19]. It must be remembered that 1 bbl oil contains approximately the same amount of energy as 170 m^3 (6000 scf) of gas, so that if the oil price is $15/bbl, then at equivalent energy rates, gas should sell at approximately $2.5 per Mscf. Total LNG costs from reservoir to the customers' jetty for the first train in the State of Qatar were estimated to be equivalent to $15.6/bbl oil, (i.e. $2.7 /Mscf gas) (upstream costs $2.2/bbl, liquefaction costs, $7.6 /bbl, transport costs $5.8/bbl), so that when the oil price is at $20/bbl LNG is a cheaper energy source but when at $10/bbl, oil is cheaper [19]. In Qatar's case condensate sales from the gas lowered the overall train costs. Transport and liquefaction costs for LNG account for ~85% of the supply cost of delivered LNG to the customer's jetty. Additional costs occur to get the gas from the jetty via gasification to the burner tip.

Although projects are location specific, GtS can claim better economics than a green site LNG plant of 500 MMscf/d [16-18]. However, the current large LNG projects have contracts typically for up to 20 years, and once the plant is built should provide stable revenues over this time period, and can cushion shorter term fluctuations in other parts of a oil field development (e.g. oil price variations). Thus competition of GtS with LNG for expansion of these large sized gas transport projects is unlikely, as too much has already been invested in LNG. On the other hand, hydrates could be attractive for such green site developments or where portable process equipment can be brought onto site e.g. mobile equipment for varying volumes of associated gas or ship for offshore, and then used until either pipeline facilities are built, or other infrastructure developed, or the gas production rate is too variable or drops below a certain value to be economic.

Small volumes of intermittent gas are not economically attractive to the major gas sellers for LNG facilities or pipelines. For these smaller markets, hydrate (and possibly CNG) can be potential economic transport methods as the quantities can be far better regulated and designed for the needs of a particular power station. GtS technology is certainly an option for handling niche markets for gas reserves which are stranded (no market), associated gas (on- or off-shore) which cannot be flared or re-injected, or small reservoirs which cannot otherwise be economically exploited.

If standard equipment and procedures could be developed worldwide then a profitable and successful small volume gas transport route could be developed when development costs would have been adsorbed in the initial projects. Even so the margins to the gas transporter will be small, unless there are other benefits, e.g. green markets for isolated islands.

Economic models have been developed for the entire hydrate supply chain for both onshore and offshore production facilities and comparisons made with LNG, GtL and CNG gas transport for bulk gas transportation [16-18]. Calculations of which is the better (cheaper and cost effective) transport scheme are fraught with danger of not always comparing like with like, ignoring the risks of higher capital borrowing for a more complicated process, differences in technical difficulty and maintenance costs, but always the GtS route is favourable. Other comparisons can be made on the capital cost of the whole plant, the risks of exposure to the investors or payback time but sometimes not much mention made of operating costs, plant upgrades during the lifetime of the project and general mechanical complications of ageing plant or political difficulties. The GtS hydrate plant is often quoted to have capital costs much lower than for LNG perhaps half. Consequently the payback period will be shorter for the same gas throughput. Clearly if hostile government or terrorist activity could occur, a project that is less costly would be favoured from an insurance point of view, particularly in terms of equipment loss. Although it is believed that the delivered cost of gas by hydrate can compete in the energy market at any scale compared to LNG, concentrating on a niche, for instance offshore associated gas or stranded onshore gas, the actual economics of gas transportation can become one element of a much bigger scenario. The extreme example is that an oil development may not proceed if there is no means to dispose of the associated gas. Selling, and hence exporting, the gas by GtS may ensure that the oil project can proceed.

Much of the analysis found in the current literature, [16-18], is for large markets and comparisons made with the large LNG plants, however there is still small volume needs for small islands or isolated communities including tourist hideaways which wants to use gas. A five star large modern hotel may need 2 MW electricity output at various times, which would need some 70 MMscf/year of gas, which is very small by world transport standards. This is only 200 Mscf/d of gas or 40 tons of hydrate per day. Transporting these sorts of 'small' quantities of gas are trivial compared with the large LNG trains, and in principle should be relatively easy and not need huge expensive specially-built ships, but there will be significant development and initialising costs.

Gas hydrates presents an alternative economic energy windows of opportunity for gas transport. Further process development with a site-specific project is needed.

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