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An Energy Efficient, Environmentally Sound Gas Production Process from Methane Hydrates

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ABSTRACT: Interest in methane hydrates as a potential source for clean hydrocarbon energy supply for the world has been steadily increasing. As a result, numerous researchers have explored different aspects of hydrates, from fundamental properties to extraction and production potential. Most of the proposed extraction and production scenarios require too much energy input, raise safety concerns or can convert only a part of hydrate to gas in a reservoir, or suffer from some combination of these deficiencies. Recently, a preliminary production study has been done to safely and efficiently extract methane from land based hydrate deposits, while maintaining a carbon neutral cycle. A novel concept of generating a point heat source, via down-hole combustion, strategically located in the hydrate deposit enables production where only about 10% of the energy content of the reservoir is used for the process. The down-hole combustion process is capable of utilizing CO2 as a diluent to adjust adiabatic temperatures to the point where methane hydrates decompose, yet $C0_2$ hydrates still form replacing methane. Feasibility calculations were made for using this point heat source as a temperature-balancing extraction process by which methane gas can be efficiently produced, while sequestering $C0_2$ in a stable environment. This paper will report on the details and results of those calculations and describe an experimental technique that will be used to validate the model and provide additional data.

1 INTRODUCTION

Natural gas hydrates are solid, non-stoichiometric compounds of small gas molecules and water. They form when methane from organic decomposition comes together with water at low enough temperatures and high enough pressures to trap individual gas molecules within atomic scale crystalline cages of water ice. They have been found as layers, nodules, and pore infillings on and beneath the sea floor in deeper waters around the world and in the permafrost areas of the Arctic.

In comparison with other important deposits, gas hydrates store an extremely large quantity of organic carbon. There are some uncertainties with regard to the global budget, yet it is believed that gas hydrate formations contain approximately 10,000 gigatons of carbon. This exceeds by far the amount of carbon stored in fossil fuels. Gas hydrates could therefore be a potential source of energy in the future when conventional fossil fuels run out. However, the role that gas hydrates may play in contributing to the world's energy requirements will depend ultimately on the availability of producible gas hydrate resources and the cost to extract them. The three main methods of hydrate dissociation for gas production include: (1) depressurization, in which the pressure is lowered to a level lower than the hydration pressure PH at the prevailing temperature;(2) thermal stimulation, in which the temperature is raised above the hydration temperature TH at the prevailing pressure; and (3) the use of inhibitors (such as salts and alcohols), which causes a shift in the PH-TH equilibrium through competition with the hydrate for guest and host molecules (Sloan, 1998).

A production technology that is energy efficient and at the same time environmentally sound has yet to be developed, for marine as well as for permafrost gas hydrates. Simple depressurization techniques or steam or hot gas injection cannot sustain continuous production. Typically, those systems rely on the perturbation of the local equilibrium to cause the hydrates to decompose and release methane as gas. While it is likely that the depressurization technique will work for a time, the consequence of the methane gas expanding from the solid phase and migrating toward the well will be the reforming of stable hydrate. Alternatively, injection of steam or hot gas suffers from significant temperature loss in transit from the surface to the hydrate region and as such generally will require nearly as much energy as is ultimately produced

In this paper we report the initial simulation results of a novel concept of locating a point heat source, via combustion of a liquid fuel and oxidant, within the hydrate region The result is a significantly lower energy requirement to produce methane Preliminary calculations indicate that energy requirements will be near 10% of the energy present in the methane hydrate This result is achieved because the amount of energy input to the local point only needs to raise and maintain the temperature of the formation by a few degrees For example, if the hydrate concentration in the formation is 10% and the temperature needs to be raised by 10°C, only 18% of the liberated energy would be required to affect that temperature rise or the efficiency would be 82% If the heat source is positioned properly, it is likely that a smaller temperature rise, about 5°C, would be needed, thus raising the efficiency To obtain an understanding of the physics governing the transport and decomposition processes, a two dimensional simulation was done by solving equations describing coupled mass, heat and reaction, time dependent behavior The FEMLAB® graphic user interface was used to generate the preliminary results reported here

2 LITERATURE REVIEW

Many groups have been investigating ways to potentially produce methane from land and sea floor based hydrate reserves(Gornitz and Fung, 1994, Laherrere, 2000, Max and Dillon, 1998, Mondis, 2003, Servio and Mahajan, 2003) Various models have been developed based on pressure reduction or temperature elevation method via hot gas injection To date we have not seen a comprehensive model that incorporates all physical phases of the dissociation from solid to liquid and gas Moreover, to our knowledge this study is the first to consider a local heat source to decompose the hydrate while simultaneously sequestering carbon dioxide in an efficient manner

Makogon (Makogon, 1974, Makogon, 1997) viewed hydrate dissociation as a moving boundary ablation process, and used the classical Stefan's equation to describe the process of hydrate dissociation In this model, a dissociation front is assumed to exist to separate the hydrate reservoir into a gas and a hydrate zone Governing equations for the movement of natural gas in both zones are set up separately A set of self similar solutions for the pressure profiles was obtained after linearization of the governing equations The water released during the hydrate dissociation was ignored in this preliminary model

Kamath used thermal stimulation for hydrate dissociation and studied the enthalpy of dissociation for hydrates of different gases Hydrates with different natural gas compositions dissociated with injection of hot water and the results showed that the rate of heat transfer and the rate of hydrate dissociation were power law functions of the temperature difference A modified Clausius-Clapeyron equation was obtained to calculate hydrate dissociation enthalpy This research also revealed additional details about the process of heat transfer at the hydrate dissociation interface(Kamath, 1983)

Durgut and Parlaktuna described a thermal stimulation method for natural gas production m a hydrate reservoir Their two-dimensional model included heat conduction and convection, and both water and gas flows(Durgut, 1996, Parluktuna, 1997)

More recently, Swmkels and Drenth studied the behavior of a hydrate capped gas reservoir using a 3-D thermal reservoir sımulator(Swınkels, 1999) They concluded that the simulation could provide insight into the natural gas production process and for economical evaluation of different production scenarios They also noted that the gas production from the hydrate cap might become thermally limited

3 MODEL SETUP

A two dimensional model was set up to simulate the heat and mass transport from the combustion point to the surrounding system The model tracked the temperature front of the heat movement through the entire formation and was coupled to a decomposition rate equation taken from literature The mam objec tive was to track the temperature front at which the hydrate decomposes to liquid water and pressurized methane gas However, it is recognized that as the temperature rises to a point where hydrate decomposition begins, there will be a condition imposed in the model such that a steady temperature is maintained until all of the phase change is complete The rate equation used is expressed on a per unit hydrate mass basis which provides versatility m terms of exploring different amounts of hydrate in the formation To simulate the time lag associated with complete hydrate decomposition, a Heavysides function has been incorporated into the model This function provides the ability to adjust the decomposition time based on the amount of hydrate present For example, if a very low hydrate loading is present, it is conceivable to imagine the time required for hydrate decomposition is very fast compared to the movement of the temperature front, thus the Heavysides function would emulate a step function Alternatively, if the hydrate loading were high, the Heavysides function would emulate more of an S-shaped curve with respect to time and may then be on the order of the temperature boundary movement time

A schematic of the hydrate reservoir system used is shown in Figure 1 The system comprises of three main zones The first zone was considered permafrost or overburden The second zone was the hydrate layer where the heat source would be placed The third zone considered was the free gas zone This is the zone, where many propose to drill to and produce gas by simply relieving the pressure This process would work, but the length of production time, and hence the ultimate amount of gas recovered is uncertain The primary limitation is the fact that as the gas expands from the pressurized free gas zone to the well the temperature will drop, thus establishing conditions to form hydrates which will limit or stop the gas flow

We are investigating whether to place the heat source at the hydrate and free-gas boundary or somewhere within the hydrate zone A first order analysis indicates the heat source should be placed at the hydrate and free gas boundary This is the position that will require the least amount of energy to maintain a steady gas flow through the well The concept relies on the principle that once the depressurization occurs near the well, only a small amount of energy is required to maintain the temperature surrounding the well a few degrees above the decomposition temperature

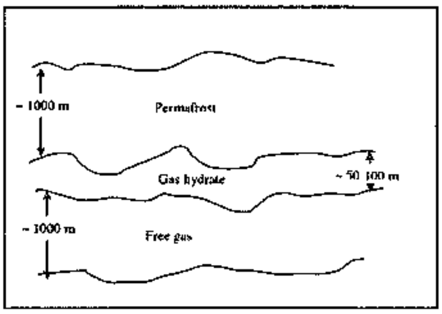

Figure 1 Conceptual schematic of matrix used in FEMLAB® simulation

The model was initially set up with the heat source in the center of the hydrate region to take advantage of symmetry and avoid a moving boundary problem This enabled us to determine the feasibility of producing methane from local heat source concept A next generation of the model currently being developed will put the heat source in an optimal position within the matrix and address the moving boundary issue The model has been developed with few assumptions and employed the fundamental laws of mass and energy conservation and Darcy's law

Consider a uniform distribution of hydrate in the porous media with initial temperature To and pressure Po The heat source is located in the center of the hydrate layer The heat source was kept as constant temperature T_c, which is the combustion temperature based on an adiabatic calculation of stoichiometric amounts of diesel fuel, liquid oxygen and liquid CO2 The temperature can be adjusted by changing the equivalence ratio (methane to oxygen ratio) or the amount of CO2 or both A gas collection well is located under the heat source in the free gas zone and has been set at a pressure of around 2 bar based on a calculation using aerodynamic head considerations

Each zone was characterized using literature values specific to each For example, the porosity of the permafrost was considered to be about 1000 times less then the porosity of the free gas zone The porosity of the hydrate zone was initially set to a value near that of the permafrost, then was reset once hydrate began to decompose to a value close to the free gas region Most values were taken from Sloan (Sloan, 1998)

The governing equations employed in the simulation are provided below The mass balance equation is given by

$$\nabla(\rho v) = \frac{-\partial(\phi S\rho)}{\partial t}$$

Where 4> is the porosity, S is the saturation, v is the velocity and P is the density

The heat transfer equation in the dissociation region may be written as

$$\nabla\ (K\nabla T) = Q - \rho C_p v\nabla T$$

Where k is the thermal conductivity.p is the methane gas density, C_p is the specific heat capacity,u is the gas velocity

The Q term is worth some discussion as it represents the amount of energy that is transferred throughout the system As such it can switch between a heat source and heat sink based on the zones properties This is the term that was expressed as a Heavysides function in the model to capture the decomposition of hydrates based on the temperture profiles achieved in matrix As the temperature front moves into a region of low temperature, the Q term represents a heat source However, as hydrate decomposes, the Q term represents a heat sink, that is that the energy required to only change the phase of the hydrate and not raise the temperature of the matrix Once all the hydrate was decomposes, the Q term transitions back to a heat source and allows the region to increase in temperature This term had the most direct impact on the results and one of the areas being focused on to better understand the transition from heat source to sink then back to source again

Once the hydrate is dissociated it was considered a two phase system of liquid water and methane gas The water resulting from the dissociation process is assumed to remain motionless and is retained within the pores of the dissociated zone This assumption puts an upper limit on the hydrate saturation The decomposed gas follows the ideal gas law It is anticipated that future results will use real gas equations such as Redlich Kwong-Soave (RKS) or another suitable expression The matrix was assumed to be a porous skeleton with properties of sandstone that did not deform before and after the hydrate decomposition and gas removal Heat effects from chemical reactions are neglected in our current model, as are changes in thermophysical properties of fluid phases (such as viscosity, surface tension, and density) due to changes in chemical composition

The governing equation for gas velocity and pressure distribution in the reservior, obtained from the Darcy's law, is given as

$$v = -\frac{k}{\mu}\frac{\partial P}{\partial x}$$

Where k is the permeability of the porous media and u is the dynamic viscosity of the methane gas The equation was coupled with heat transfer equation to get the final temperature disturbution and velocity profile The programmed in Heavisides function is used to switch properties of the computional domain at the heat front when the temperature reaches the dissocation temperature Currently the model does not take into account the effect of the combustion gases and CO_2 diluent throughout the matrix Although the model setup has a few simplifiying assumptions, it does provide insight into the feasibility of placing a heat source to locally heat the hydrate to produce gas At present, we are using the prelimnary calculation results to guide subsequent experiments to better understand the issues surrounding this concept

4 RESULTS

Presented below are the simulation results from the temperature, pressure and velocity profiles for the steady state conditions Also depicted in the Figures is a simulated well bore that would be used to extract the methane gas As described above, the pressure of the well bore was calculated to be near 2 bars, thus creating a pressure sink and establishing the desired gradient for gas flow from the decomposed hydrate and the free gas The surrounding pressure around the well bore is lower than the far field pressure This condition allows for the gas released in the hydrate to migrate toward the well, thus allowing the entire hydrate zone that is decomposed to drain Since the flow is highly restricted in the upper sediment layer and the regions of stable hydrate the desited flow pattern is established The maximum flow velocity is through the decomposed hydrate and freAgas region 0 008 m/s, which is two orders of magnitude higher than the upper limit of fluid velocity in the over burden and stable hydrate zones This higher velocity is attributed to the high pressure gradient at the heat source

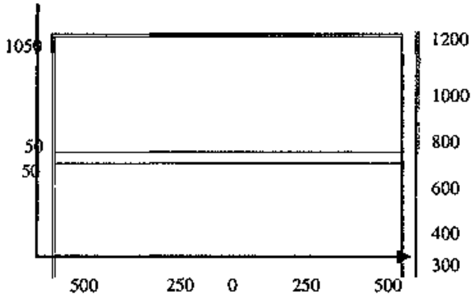

Figure 2 Complete calculation domain

Figure 2 shows the temperature profile for the entire calculation domain to provide a sense of the size of the local heat source in relation to the affected region The scale of the simulation should be noted at this point The horizontal scale was taken to be 500 units and the vertical scale was taken to be 2000 units with the hydrate layer being about 100 units The heat source is only 1 unit in diameter These units can be translated into meters if desired and gives an idea of the influence such a small heat source has in the overall matrix

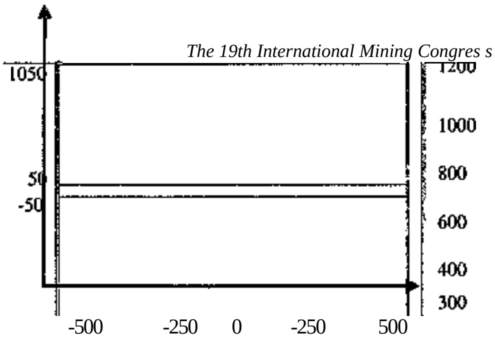

Figure 3. Temperature Distribution

Figure 3 shows a magnified view of the temperature distribution as a funtion of the two dimensional distance. Here one can now see the locatation of the well to extract the gas. As expected the heat front radiates out and exponentially decays to the far field temperature, which was taken as a function of pressure based on information from United States Naval Research Laboratory (2004). The far field temperatures were taken as -25°C at the top surface, 25°C at the bottom surface and the side surfaces followed the temperature gradient as dictated by the pressure gradient mentioned above.

The pressure distribution and flow pattern are shown in the Figures 4 and 5. The point heat source was simulated as a constant energy input as described above. Very near the heat source, the pressure is high due to the conditions that are setup by this process. Not only has the hydrate decomposed completely, but the methane gas and water are now being superheated and thus result in a local pressure buildup. This pressure will not reduce until gases are withdrawn from the well bore, positioned in the free gas zone in this simulation. Because the permeability is small compared to the free gas zone that is below the hydrate layer, it is hard for the released the gas to get through to the overburden and as a consequence, the pressure builds up at the interface between hydrate layer and the upper sediments. This can bee seen in Figure 4.

In Figure 5, arrows represent the velocity profile of the methane gas only. The length of the arrows are proportional to the velocity. In the center of the heat source the gas maintains a fairly high temperature and thus sets up a steep pressure gradient, so the gas velocity is high. Moving away from the heat source, the temperature drops which results in a commensurate drop in pressure. As the temperature drops below the hydrate decomposition temperature, the pressure gradient becomes negligible and gas flow essentially stops. This is considered the far field condition, which is maintained throughout the simulation.

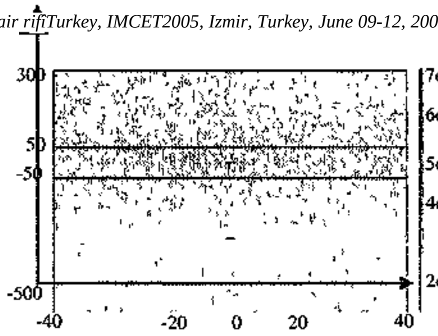

Figure 4. Pressure Distribution

The velocity distribution of the methane gas is shown in Figure 5. The flows that are established result from the pressure gradients that are set up from the local heating and dissociation of the hydrate. The right hand scale is velocity in meters per second. The interesting thing to note is the region of influence the small point heat source has throughout the matrix. Although the point heat source is only 1 unit in diameter, it is causing methane gas movement 40 units in either direction.

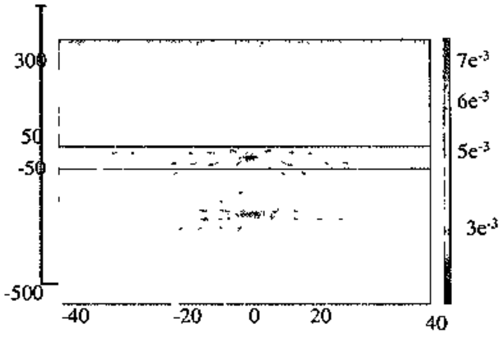

Figure 5. Velocity Distribution

Now one can see why applying a local heat source at the properly located position within the matrix is so efficient. Not only is all the energy required to dissociate the hydrate release where it is needed, but also the far reaching impacts the source has make it very effective. Not shown in Figure 5 is the far field region where the velocity goes to zero because the temperature is at the reservoir temperature and the pressure gradients are extremely small.

CONCLUSIONS

The simulation results give us a preliminary understanding of the down-hole combustion process, which has the potential of being implemented efficiently, and safely to produce methane from methane hydrate formations. We have observed that:

1. The high temperature created by local combustion establishes a reasonable temperature gradient in the hydrate layer within a feasible time.
2. The heat flux supplied by high temperature allows continuous dissociation of hydrate.
3. The high temperature of the combustion also enhances the gas flow in the porous media, which will in turn helps to improve the heat transfer and gas collection.

6. FUTURE EXPERIMENTAL WORK

To assess the potential for a viable gas production process based on in-situ controlled combustion coupled with $C0_2$ sequestration, we developed a three- phase experimental procedure:

Phase I: Construction of the test apparatus

We have completed the design of a test apparatus. This apparatus consists of a chamber where hydrate is formed by adjusting temperature and pressure. To simulate hydrate bearing formations commonly seen in various exploration sites including the Beaufort-Mackenzie Basin, fine grained (~lmm diameter.) silica and water mixture is to be used. The temperature and pressure are continuously monitored and regulated in order to replicate in-situ thermodynamic equilibrium conditions. Initially a point heat source will be imbedded in the middle of the hydrate block. During the first phase, the local heat source will be electrical. In the subsequent phases of the experiment, this will be replaced by a pipe through which oxygen and $C0_3$ mixture will be injected to provide targeted stoichiometric mixtures for combustion for local heat generation. A series of various mixtures will be explored to find optimal conditions for combustion, temperature, production rates and $C0_2$ sequestration. Near the heat source there will be a number of production pipes at varying distances. As heat is applied to the middle of the hydrate formation, the local dissociation will take place. Gas flow will be monitored in the production pipes at various controlled outlet pressures. Water with gas will also is expected to flow out. This water will be returned to the system in order to maintain the mass balance and simulate what may have to be done in the field. In the experiments make-up water will be injected from the water supply line.

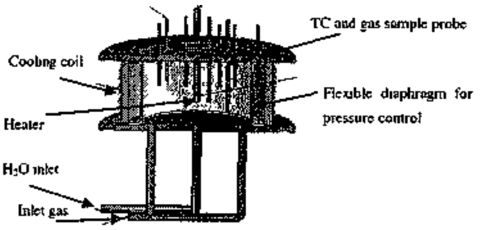

Figure 6. Interior of testing apparatus

This apparatus will be used for our first phase test. As shown in Figure 6, the device consists of a chamber where hydrate is formed by regulated temperature and pressure. The chamber will be filled with the sand-pack porosity from 30 to 45%, which is a typical range for the permafrost region in Alaska (Bradley, 1989). The methane gas and water is fed into the chamber from the bottom of the chamber.

On the top of the chamber we inserted a number of tubes that will house a thermocouple and work as gas sample collectors. In order to measure the distribution of gas flow and the temperatures, the thermocouples and gas sample probes are uniformly distributed on the radial and circumferential directions. As shown in the sectional view (Figure 6) of the chamber below, probes are also located at different depths along the axial direction.

Using this experimental apparatus it will be possible to

- Verify the feasibility of gas hydrates dissociation by down-hole fire flooding.
- Understand important characteristics such as temperature and pressure profiles for methane hydrate formation and dissociation in pure water system as a reference.
- Obtain the relevant data to develop the models for methane hydrate dissociation by combustion method.
- Maintain constant pressure for the duration of the experiment to approximate far field conditions.

Phase II Experiments

Once the initial shakedown and feasibility tests are completed, we plan to expand the effort. In these experiments we will operate with simulated atmospheric pressure at the well head while maintaining underground pressure and formation temperature except where the local heating takes place. This will allow us to investigate the conditions for hydrate formation due to sudden pressure loss at the well head. We will also implement several controlled outlet pressure levels while maintaining the underground pressure. The purpose from this type of experiment is to develop parameters for continuous gas production by controlled local heating and pressure control at the well head. At the outlet locations water is expected to flow out with methane. It will be necessary to separate the water and re-inject into the system to maintain the mass balance. In these experiments the water produced will be measured and equal amount of water will be injected from the bottom of the experimental apparatus

Phase III Experiments

Extending the work further, the full concept of methane production from hydrates with simultaneous carbon dioxide sequestration will be tested These experiments will include $C0_2$ injection while CH_4 is being extracted from the system Pressure controls m Phase II experiments will also be used in here In addition to maintaining the water present in the experimental apparatus by injecting water to make up the losses at the methane production points, $C0_2$ will be injected to replace CH_4 extracted Injection ports will be controlled so as to maintain overall system in situ pressure and allow well head and well bottom pressure drops Extracted CRt and sequestered $C0_2$ will be metered in order to estimate the system capacity for extraction and sequestration Even after exhaustion of all extractable CH_4 is done, $C0_2$ injection will continue by capping extraction wells and system pressure will be monitored As $C0_2$ hydrates form, pressure should drop because of volume reduction Experiments will terminate when no additional $C0_2$ can be injected at the fixed system pressure We will repeat these experiments at various system pressures and temperatures and collect extraction and sequestration data as a function of these two major system parameters

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