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INVESTIGATING THE PRODUCTION OF METHANE GAS FROM METHANE HYDRATES THROUGH FLUORINE GAS INJECTION

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ABSTRACT

It's no news that a major limitation of existing methods for producing methane gas from methane hydrates is the large scale productivity. Methane hydrates is a novel energy resource amply distributed around the globe. These energy source lies in huge proportion in their sediment and have the possibility to counter future energy demands. This paper examines the feasibility of recovering methane gas by the injection of fluorine gas. In this analysis, existing production methods and limitations, reservoir assessment, fluorine reactivity with methane hydrates, and efficient productivity are considered. Fluorine gas is highly electronegative which makes it very reactive to cause a destabilization of methane hydrates equilibrium position to methane gas and water. Processes such as wurtz reaction, electrolysis, and cracking are followed to efficiently recover the liquefied gas hydrates solution.

1. Introduction

Since it discovery, methane hydrates have generated lot of response in terms of research from different institutions around the world. The prospect for methane hydrates is evident in it clean energy supply and enormous in-place volume. Gas hydrates are whitish balls located in several depth in deepwater favoured by conditions such as high pressure, low temperature, and organic detritus. One unit volume of methane hydrates at a pressure of one atmosphere produces about 160 unit volume of methane gas – thus gas hydrates are very energy – dense reservoir of fossil fuel [1].

Despite it scrupulous amount in deposit, there exist series of production challenges in their recovery. Historical attempts to produce natural gas from these structures such as the one at Messoyakha Field showed that natural gas hydrate reservoirs pose different problems than any other conventional or unconventional gas reservoirs and should be handled differently [2]. By virtue of factor such as farther depth of hydrates formation, methane gas hydrates has a lesser density compared to conventional formation with shallow depth. Conventional gas reservoir consist primarily of gas that can flow in the pores of the reservoir rock [3], while unconventional gas reservoir are sediment containing gas hindered from migration.

This is the major reason efficient production technique is required to release this methane gas from it cage of solid water lattice. While highly speculative for a fossil fuel resource that has essentially zero commercial production at present, interest in hydrates has increased in some part of the world where other source of energy are less available or more expensive [1].

There are three methods currently for producing gas from methane hydrates. These are steam injection, depressurization and chemical stimulation. These methods involves altering the equilibrium position in order to release methane gas trapped in subsurface. Thermal stimulation involves preparing steam or hot brine at the surface before injection into the wellbore to cause a dissociation of the hydrates bearing. A major limitation using this method is heat loss. Steam prepared above 200 degree Celsius at the surface is being neutralized by the occurrence of deepwater and the farther depth of gas hydrates deposits, thereby making it very inefficient in producing methane gas. Depressurization method reduces the pressure of solid methane hydrates which enable its formation by pumping the drilling fluid out of the wellbore to the surface. Though, depressurization method is quite efficient and more economical because of lesser need for an external heat source and hydrate dissociation influenced by heat conduction from external formation, it suffers a prevailing limitation such as endothermic reaction which cause a decrease in reservoir temperature and slower rate of dissociation. Chemical stimulation uses chemical as methanol, ethylene glycol and di – ethylene glycol to enable possible hydrate dissociation. This method is challenged by economics because methanol and ethylene glycol are expensive chemical and large quantities of these chemical are required for efficient methane gas production.

In order to fully develop methane gas reservoirs, it is pertinent to understand the mass transfer through methane hydrates layer. Fluorine is known for its highly electronegative nature and can influence rapid dissociation of methane hydrates. The objective of this study is to investigate the process of producing methane gas efficiently by injecting fluorine gas to stimulate the methane hydrates and possibly cause dissociation at constant temperature and pressure conditions.

2. Methodology

2.1. Release of microwave

Microwave technology release sustainable amounts of heat which can melt the solid hydrate lattice. The temperature which enables this phenomenon range from 273 kelvin and above which help decline the period required for dissociation. The decomposition of hydrates with microwave were studied by Rogers [5]. The study showed that microwave heating was a very effective method in enabling proper dissociation needed in the recovery of methane gas. It was concluded that NGH will dissociate when the intensity was more than a certain value, because the movement of the molecules in the system was increased by microwave [6]. An alternative method for performing microwave assisted organic reactions, termed "Enhanced Microwave Synthesis" has also been used, where external cooling is applied to the reaction vessel while simultaneously administering microwave irradiation [7]. This enables the stabilization of the hydrates' temperature while microwave heating takes place.

2.2. Injection of fluorine gas

The injected fluorine gas react with methyl radical (CH_3) of methane gas. The product of this reaction is methyl – fluoride (CH_3F) and liberated fluorine. This reaction is very vigorous as well very reactive and exothermic which releases subsequent amount of heat and a reaction enthalpy of about -431KJ/mol. The reaction paves way for energy required in the recovery of liquefied gas hydrates. Standard operating pressure should be strictly adhered to in order to prevent explosions which arises from the high reactivity of fluorine by diluting the reaction with helium gases.

$$CH_3 + F_2 \rightarrow CH_3F + F^*$$

2.3. Recovery of liquefied gas hydrates solution

The recovery of methane gas can be recovered following the steps below:

- Step 1: Wurtz reaction
- Step 2: Electrolysis
- Step 3: Cracking

2.3.1. Wurtz reaction

The product of fluorine gas injection methyl – fluoride (CH3F) needs to be broken down. Methyl – fluoride bond is very strong which is the reason wurtz reaction needs to be used. By virtue of wurtz reaction, methyl – fluoride (CH3F) is heated in the presence of sodium (Na) and ether to produce sodium fluoride (NaF) and ethene (C2H6), a heavier hydrocarbon.

$$2CH_3F + 2Na \rightarrow 2NaF + C_2H_6$$

The success of the reaction is ensured by the following:

- The rate of reaction should decrease in the presence of oxygen (O_2) which proves the mechanism is correct
- The solvent (ether) must be very dry so that the sodium doesn't react with the Deepwater
- The reaction can only produce 2C (C_2H_6)
- The entropy of the reaction is less than 0

2.3.2. Electrolysis

Sodium fluoride (NaF) compound is broken down into sodium (Na) and fluoride (F) by electrolysis of water. This is because water easily undergo oxidation and reduction compared to fluoride.

$$NaF \rightarrow Na + 1/2F_2$$

2.3.3. Cracking

This involves the breaking down of ethene to methane gas. It can be done by either catalytic induced or steam induced cracking. Catalytic induced requires the presence of a catalyst such as zeolite and subjected to a temperature of about 550 degree Celsius while steam induced don't require the presence of a catalyst but a higher temperature of about 800 degree Celsius.

$$C_2H_6 \rightarrow 2CH_4$$

3. Advantages of this method compared to other production techniques

- It increases the permeability and porosity of the rock governing the methane hydrates
- Huge reduction in disaster related to rig floor or drill floor
- Rapid and selective heating
- Catalyse chemical reactions
- Methyl – fluoride is not an ozone depleting chemical compound

4. Challenges associated with fluorine gas injection recovery method

- Injection problem which arises from the electronegative and reactive nature of fluorine
- Mass transfer of methyl – fluoride solution
- Method of recovery is quite complex
- Storing fluorine gas require a special suction tank that doesn't react with it

5. Conclusion

The clean energy nature of methane hydrates, versatility of it usage and spectrum of its deposit has supported concurrent research in efficient recovery methods. Gas hydrates are solid mixture of methane gas and water containing about 160 time the volume of methane gas at standard conditions. Condition as temperature below 295 Kelvin and pressure above 3000 Kilo Pascals favours it formation. Problems as heat loss, decrease in reservoir temperature and economics affects the wide scale recovery using the present day technique. The electronegative nature and high reactivity of fluorine gas allow for selective heating and catalyse reaction for producing methane gas from gas hydrates. The procedure involves firstly releasing microwave technology at a frequency of 2450 Mega Hertz to injection of fluorine gas and possible recovery of gas hydrates solution by application of; wurtz reaction, electrolysis and cracking. However, careful handling of fluorine should be ensured to prevent hazards and efficient recovery of methane gas.

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