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Evaluation of Chemical Inhibitors on Methane Production: A Critical Review.

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***Abstract**: Chemical inhibitors are used in decomposition of methane hydrate to produce methane and this process involves the injection of chemical inhibitors that changes the equilibrium conditions for hydrate formations. Most applicable chemicals are such as methanol, ethanol or brine. In this research work, we discuss the evaluation of chemical inhibitors on methane production. In this paper different literatures reviews have been visited concerning evaluation of chemical inhibitors on methane production and this have been done through consulting internet search in which secondary data were extracted. It was observed that most literatures do not contain the knowledge on the evaluation of chemical inhibitors on methane production. It was recommended that in the future, the research work on the evaluation of chemical inhibitors on methane production needs to be done by performing the surveys on the cost analysis of these chemicals inhibitors, environmental effect on its uses and the favorable conditions fit for these chemical inhibitors.*

Keywords— chemical inhibitors, methane hydrate, hydrate formations, natural gas hydrate, thermodynamic, phase equilibrium, hydrate stability

1. INTRODUCTION

Sedimentary hosted gas hydrate is confined within pores and is therefore immobile. To be able to produce and recover the methane trapped in the structures of the hydrate, the natural gas hydrate (NGH) have to either dissolve or be introduced to a more thermodynamically stable hydrate that will swap place with the methane. Existing technology can be applied to produce methane from NGH.As proposed by the author in [1], these technologies to recover methane have not changed much since the early 1980's and one of it is injection of chemical inhibitors.

Chemical inhibiting is the process of injecting chemicals in the reservoirs to dissociate the hydrate. Some kinds of thermodynamic inhibitors which are most applicable are such as; methanol, ethanol, or brine. The injection of thermodynamic inhibitors leads to change the formation condition of hydrate phase equilibrium,[2]. The formation of hydrate stability temperature will be reduced or stable pressure will be increased, making the hydrate system unstable and the hydrate decomposes accordingly.

The advantages of such kind of method includes the hydrate prevention flow assurance and gas production rate within a very short of time. However, from the economic point of view, this method is not promising as inhibitors are very expensive and also causes environmental pollution. The only main obstacle caused by this method is the low permeability of hydrate bearing-regions, which hinders the diffusion of injected chemicals.

By lowering the activity of hydrate formation water, the thermodynamic inhibitors make the hydrate formation condition more demanding. Thermodynamic inhibitors mostly used to promote the hydrate decomposition, improve the decomposition rate of gas hydrate and increase gas production in the process of exploitation of natural gas hydrate.

Many researches have been carried out, the effect of inhibitors injection in the production of natural gas from gas hydrate. The authors in [3], investigated the behaviors of hydrate dissociation pressures for methane or ethane containing aqueous triethylene glycol with an isothermal apparatus. Englezos *et* al in [4] , studied gas hydrate formation/decomposition conditions in electrolyte solution. The authors in [5, 6] carried out a systematic study to predict the hydrate stability boundary conditions for system with salt and organic inhibitors. As illustrated in figure 1, hydrate reservoirs are heated by injecting thermodynamic inhibitors.

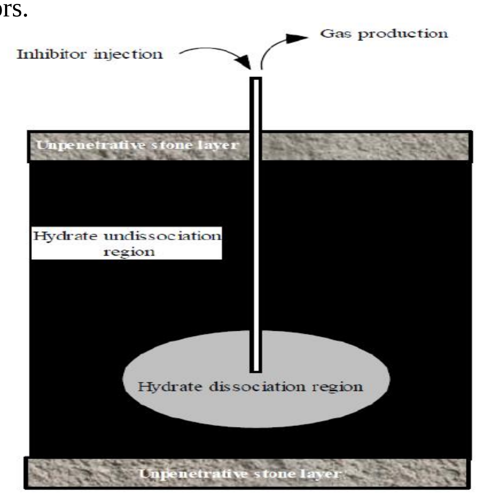

Figure 1: Gas production from hydrates by thermodynamic inhibitors [7].

Besides, the effects of type and concentration of inhibitors on hydrate dissociation were studied by many groups. And it has been found that, with the increase of the volatility of inhibitors, the inhibiting effect reduces, which is attributed to the fact that highly volatile inhibitors are usually in the gas phase, [8].

In chemical engineering analysis, the volatility of methanol is higher than that of ethanol and ethylene glycol. When the concentration of methanol and ethanol is less by 5 wt%, their injection could promote the formation of hydrate. And the authors in [9],came out with comparison of ethanol to ethylene glycol and stated that, ethylene glycol has lower volatility and stronger hydrogen bonding with water, therefore, it is more beneficial for recycling than ethanol. Also it is known that, the inhibiting effect of electrolyte on hydrate is always different in comparison to both ethanol and ethylene glycol.

When methanol is used as inhibitor, the formation temperature increases as the pressure decreases and when electrolyte ($CaCl_2$) solution used as inhibitor, with the increase of pressure, the inhibiting effect decreases first, to a minimum point and then increases slightly. It is pointed out that, pressure influences much on inhibitor performance, [10].

The aim of this research paper, is to visit different literatures on the evaluation of chemical inhibitors on methane production, in which studies about chemical inhibitors and its evaluation on methane production are extensively visited.

2. BACKGROUND AND LITERATURE SURVEY

The authors in [11], conducted an investigation into the laboratory method for the evaluation of the performance of kinetic hydrate inhibitors using superheated gas hydrates and the results showed that, hold times were shorter than using non-superheated hydrate test methods, but they were more reproducible with less scattering and sometimes the results varied between different size autoclave equipments.

Duchateau *et* al in[12], performed the evaluation of kinetic hydrate inhibitor (KHI) performance, using high-pressure autoclaves and the results showed that, the comparison between the subcoolings ΔTsub,lim (difference between the hydrate equilibrium temperature and the crystallization temperature at hydrate reformation when a constant cooling rate was applied), measured with and without an additive at hydrate reformation was a convenient way to estimate the potential of the additive to inhibit hydrate growth.

According to the authors in [13], studied the methane production in the interstitial waters of sulfate-depleted marine sediments and found that, methane production does not occur until dissolved sulfate is totally exhausted.

Storr *et* al in [14], conducted a combined theoretical/experimental study into a new class of kinetic inhibitor of gas hydrate formation and they found that, the inhibitor was bifunctional, with the hydrophobic end being compatible with the water structure present at the hydrate interface, while the negatively charged functional group promotes a long ranged water structure that was inconsistent with the hydrate phase; the sulfonate-induced structure was initiated to propagate strongly over several solvation shells.

The authors in [15], conducted the study focused on the application of batch tests to determine the maximum specific Anammox activity(SAA) in different conditions in which the batch tests were based on the measurement of nitrogen gas production and they found that, the developed batch experiments were suitable to establish not only the maximum SAA of certain sludge but also the inhibitory effects of certain tested compounds.

The authors in [16], studied the potential rates of both methane production and methane consumption over three orders of magnitude and their distribution and the results verified that, variation in potential methane oxidation could be related to site characteristics with a model of methanol trophic biomass.

Chen *et* al in [17], conducted the study on the kinetics of methane fermentation and on their study they found that, methane production data under steady state can be used to study the kinetics of the methane fermentation and the constants determined were maximum specific growth rate, kinetic constant ,and finally attainable methane production.

The authors in[18], conducted the evaluation of kinetic hydrate inhibitors (KHIs) in laboratory high-pressure cells and they found that, the presence of these precursors strongly increases the repeatability of results compared with systems containing "fresh water" and allows unambiguous discrimination between blank (uninhibited system) and KHI tests.

The authors in[19], examined natural hydrophobic amino acids as novel kinetic hydrate inhibitors (KHIs), and investigated hydrate inhibition phenomena by using them as a model system and they found that, perturbation of the water structure around KHIs shows a critical character in hydrate inhibition.

Cha *et* al in [20], performed the hydrate formation characteristics through investigation with synthetic natural gas at different mono-ethylene glycol (MEG) concentrations by measuring hydrate onset time and sub-cooling temperature and also investigated the hydrate formation in the presence of both MEG and poly-vinyl pyrrolidone (PVP),the results suggested that it might be feasible to incorporate the kinetic inhibition performance of MEG into present hydrate inhibition strategy to manage the hydrate risk.

Peytavy *et* al in [21], presented the work deals with the kinetics of methane hydrate formation which was studied in a laboratory loop where the liquid blend saturated with methane was circulated up to a pressure of 75 bar and the results showed that, the tested kinetic inhibitors and dispersant agents could be effective for the transport of multiphase streams during a short period without plugging.

The authors in [22], Investigated the influence of pH and ammonium-nitrogen on methane production in a high-solids sludge digestion process by using a mesophilic batch digester fed with a sludge cake and the simulated results revealed that, the methanogenic activity decreased with an increase in ammonium-nitrogen, dropped 10% at an ammonium-nitrogen concentration of 1 670 to 3 720 mg/L, dropped 50% at 4 090 to 5 550 mg/L, and dropped to zero at 5 880 to 6 000 mg/L.

According to the authors in[23], the methane production can be represented by the following kinetic decomposition reaction;

$$CH_4.\mathrm{n}H_2\mathrm{O} \pm \mathrm{Heat} \rightarrow + CH_4 + \mathrm{n}H_2\mathrm{O}$$

The methane production from methane hydrate is regarded as endothermic equation, since there is a gaining heat during the decomposition process, in which $CH_4.\mathrm{n}H_2\mathrm{O}$ is the methane hydrate, and n is the corresponding hydration number which range between 5.75-7.4.

The authors in [24], explored inhibitory effects of condensed tannins (CT) on methane, hydrogen, total gas and volatile fatty acid (VFA) formation for the forage legumes *Lotus pedunculatus* (also known as *L. uliginosus;* CT 0.10 of DM) and *Medicago sativa* (lucerne; CT < 0.001 of DM) in the presence and absence of polyethylene glycol (PEG; a tannin binding reagent) and 2-bromo-ethylsulfonic acid (BES; a methanogen inhibitor) and they found that, CT action on methanogenesis can be attributed to indirect effects via reduced hydrogen production (and presumably reduced forage digestibility) and via direct inhibitory effects on methanogens.

Hansen *et* al in [25-28], studied the method for the determination of methane potentials of solid organic waste and the results showed that, the determination of methane potentials was a biological method subject to relatively large variation due to the use of non-standardized inoculum and waste heterogeneity.

3. METHODOLOGY

The methodology applied in this research was an 'Internet Search', in which the research visited different sources on the internet to find evidence and facts about the evaluation of chemical inhibitors on methane production. Where possible websites of the specific resources were consulted, for instance websites of some journals which put materials in HTML format only rather than pdf or word document. The visited literatures are found on the internet. So generally secondary source of data were mainly used in a large portion of this study to come up with the conclusion.

4. DISCUSSION

Through visited literatures that have been conducted for evaluation of chemical inhibitors on methane production, many authors discussed on how to use chemical inhibitors on methane production in which they didn't surveys much more on their effects on methane production . Also on the theoretical/experimental study done on chemical inhibitors on methane production, no much more information concerning the environmental effects especially at what extent these chemical inhibitors affect the environment in its uses and how to avoid such effects during the production case.

Moreover, no much more information concerning the economic value of such chemical inhibitors in its uses. Also no much more information on what is better kind of chemical inhibitors that are most applicable ones, among the methanol, ethanol or brine as mentioned by many authors. Also no much more information concerning the favorable conditions fit for these chemical inhibitors, to show the effectiveness when the environmental conditions changes.

5. CONCLUSION AND FUTURE WORK

In this paper, the author visited different literatures about evaluation of chemical inhibitors on methane production, and the results from most of the literatures concentrated on the hydrate production using chemical inhibitors, gas hydrate formation condition prediction with chemical inhibitors, and theoretical/experimental production of methane by using chemical inhibitors, but they didn't talk on the evaluation of chemical inhibitors on methane production.

In the future, the author recommends on performing the research on the evaluation of chemical inhibitors on methane production, in which more surveys on their effects of chemical inhibitors on methane production including its environmental effects based on the extent and on how to avoid such effects during the production process.

Also more study on the economic point of view of these chemical inhibitors on methane production, should be conducted and the study on the kinds of chemical inhibitors on methane production and the favorable conditions fit for these chemical inhibitors should also be done to clarify its usefulness on methane production.

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