

Primarily Study on Gas Hydrate Formation Promoters: The Influence and Efficacy of Different Promoters and Introducing Xanthan Gum as a Novel Promoter

Sokpheapnika Chea¹⁾, Chul-Whan Kang²⁾ Gye-Chun Cho³⁾

^{1), 2), 3)} Department of Civil Engineering, KAIST, Daejeon 305-600, Korea

¹⁾ chsnika@kaist.ac.kr, ²⁾ jeremoss@kaist.ac.kr, ³⁾ gyechun@kaist.ac.kr

ABSTRACT

Natural gas hydrates are solid ice-like substances in high-pressure, low-temperature environments, commonly occurring beneath the seafloor or in frozen sediments—the first hydrate formation in the petroleum and gas industry as an obstacle in pipelines reducing the flow rate and bringing economic impacts. Several methods have been used to eliminate the presence of this gas hydrate, and one of them is to use additives. However, recently the role of the inhibitors has been used reversely for newly found applications., where the formation of gas hydrates is beneficial, like natural gas storage and transportation, gas separation, and sequestration. This paper focuses on a comprehensive review of additives promptly promoting gas hydrate formation. Moreover, this paper also suggested xanthan gum as a novel promoter. Due to its properties, such as having high specific areas with varying charges and different sizes that could interact with fine soil (sand, silt, and clay), we expected it to function as a promoter and positively affect the development of research on enhancing gas hydrate formation rate.

1. INTRODUCTION

Rapid global population growth has increased the attention to preparing future energy. Gas hydrate has become the main topic due to its massive amount worldwide and its ability to store natural gas. For $1m^3$ of gas hydrate, there is approximately $200 m^3$ of natural gas at standard temperature and pressure stored in hydrates (Kim et al., 2004).

Gas hydrates, solid crystalline structures formed by water and gas molecules, initially pose significant challenges in various industries due to their potential to clog pipelines, restrict flow, and induce equipment failure in the past. Inhibitors have been used to prevent gas hydrate formation and mitigate associated risks. However, recent advancements in research have unveiled a surprising and innovative twist - specific inhibitors are now being utilized as promoters, revolutionizing the approach to gas hydrate control. The term "promoter" refers to a substance that actively induces or accelerates a specific chemical reaction, in this case, the formation or dissociation of gas hydrates. While traditionally, inhibitors were deployed to hinder gas hydrate

crystallization, their ability to function as promoters presents a new perspective on tackling hydrate-related issues.

Promoters in gas hydrate control can be broadly classified into two categories (Q. Nasir et al., 2020): conventional and emerging. Conventional promoters have been widely explored, but they have their limitations. One of the most significant challenges with conventional promoters is the formation of foam during application (Sowa et al., 2014), leading to operational complexities. In contrast, emerging promoters have shown promising results in gas hydrate control (Q. Nasir et al., 2020). These innovative agents possess remarkable efficiency in promoting gas hydrate formation or dissociation, rendering them potent alternatives to conventional promoters. However, a critical drawback hindering widespread adoption is their elevated cost, making large-scale implementation challenging.

This paper aims to comprehensively review conventional promoters like Sodium Dodecyl Sulfate (SDS) (H. Kakati et al., 2016) and emerging promoters such as Icemax® & Drift® (J.-H. Sa & A.K. Sum et al., 2019) and Amino Acid (Liu et al., 2015; Veluswamy et al., 2016) and suggest a new biopolymer promoter. The idea behind this study originated from whether a biopolymer could function as an additive, induce nucleation, and promote hydrate formation, and the first target is Xanthan gum.

2. PROMOTERS CLASSIFICATION

2.1 CONVENTIONAL PROMOTERS

The Sodium Dodecyl Sulfate (SDS) surfactant was introduced as a conventional promoter to increase the hydrate formation rate. Zhang et al. studied the role of SDS in methane Hydrate formation in a non-stirred reactor and discovered that SDS accelerates hydrate growth (J.S. Zhang et al., 2007). Yoslim also reported that adding SDS increases gas consumption by approximately 14 times compared to pure water (J. Yoslim et al., 2010). Another study that has been done by Kakati et al. Zinc oxide (ZnO) and Aluminum oxide nanoparticles were used with SDS, functioning as a stabilization. 0.03% (wt) SDS has been added to the aqueous solution. The results showed that adding both (ZnO and Aluminum oxide) nanoparticles increases the gas consumption rate and the amount consumed. The amount of gas consumed in the presence of these particles has risen by almost 121% compared with that of pure water systems (H. Kakati et al., 2016).

However, a drawback in using SDS as a promoter is that it must be mixed with other nanoparticles to maximize efficiency. As a result, the cost of incorporating it also doubles, which can be a limiting factor. Also, conventional promoters like Tetrahydrofuran (THF) and sodium dodecyl sulfate (SDS) their commercial usage is restricted due to the undesirable foam formation they cause.

2.2 EMERGING PROMOTERS

2.2.1 Icemax® & Drift®

J.-H. Sa and A.K. Sum have introduced two types of kinetic promoters. One is a protein-type promoter called "Icemax®," and the other is a surfactant-type promoter known as "Drift®." (J.-H. Sa & A.K. Sum et al., 2019). These promoters increase gas solubility, the lowered surface tension of the gas-liquid interface, and the capillary-driven water supply. Two types of experiments have been conducted, ice-nucleation test and hydrate formation under high shear test.

When subjected to high shear conditions, the measurements of sl CH_4 hydrate and sl CH_4/C_2H_6 hydrate formation kinetics demonstrate that incorporating ice-nucleating additives can significantly boost the rate of hydrate growth and increase the amount of hydrates formed at a stable rate. One such effective additive is Drift®, which is surfactant-based. It dramatically improves hydrate kinetics, especially under non-stirred conditions, leading to an 18-fold increase in water conversion compared to hydrate formation without additives. Hydrate formation showed a mass transfer limitation without additives at the gas-liquid interface. Drift® functions by reducing the interfacial tension, promoting faster hydrate growth by improving the physical contact between phases. Under low shear conditions, the enhanced formation kinetics facilitated by ice-nucleating additives are confirmed through the measured subcooling required for hydrate formation in the rock-flow cell. Icemax® is particularly effective in inducing hydrate formation by providing additional sites for heterogeneous nucleation. Both Drift® and Icemax®, as observed through the visual characterization in stirred cell and rock-flow cell experiments, accelerate hydrate kinetics, resulting in softer and more porous hydrates.

2.2.2 Amino Acid

The amino acid was first introduced as a promoter by Liu (Liu et al., 2015). Liu et al. investigated methane hydrate formation with different amino acids in detail. It was mentioned that leucine amino acid is the best promoter for methane hydrate formation and kinetic promotion. Even though the promotion effect of leucine was established in the work of Liu et al., the hydrate formation mechanism needed to be better understood, and morphological changes during hydrate formation were not available. Due to this reason, Veluswamy decided to improve by investigating the formation of hydrate using leucine amino acid at different concentrations and presenting morphology observation (Veluswamy et al., 2016). Moreover, SDS with the same concentration was also used in the hydrate formation test to compare the hydrate formation of amino acids with conventional surfactants.

Different concentrations of amino acids, 0.2, 0.3, 0.4, and 0.5 wt% using 1 mL of the solution at the same experiment condition of 10 MPa and 275K. Throughout the experiment, it was observed that using 0.2 wt% or lower had no promotion effect on hydrate formation. On the other hand, during the hydrate formation process with a 0.3 wt % leucine solution, a noticeable methane bubble with unique characteristics was observed during the hydrate growth phase. When the leucine concentration exceeded 0.3 wt %, the methane hydrate growth exhibited a mushy and rapid behavior, leading to significantly faster kinetics. The conventional surfactant exhibits better kinetics for the comparison between the two promoters. However, there is foam formation which is a potential drawback to the use of surfactants for hydrate-based applications. In contrast, foam could not be found in the hydrate formation test using amino acid as a promoter.

3. INTRODUCTION OF NOVEL PROMOTER, BIOPOLYMER

The utilization of biopolymer as a promoter is motivated by its exceptional properties. As a soil skeleton, biopolymers provide a stable framework for soil structures. Their high specific area, diverse charges, and particle sizes enable efficient interactions with fine soil particles, enhancing soil properties (J.Huang et al., 2021). Moreover, biopolymers have a proven track record of success in soil improvement and stabilization, validating their efficacy as promoters (T.Zhang et al., 2020). Beyond their practical benefits, biopolymers offer a significant advantage in terms of environmental friendliness (J.Huang et al., 2021), resulting in reduced pollution compared to conventional alternatives. Another appealing aspect is their cost-effectiveness, making them a relatively inexpensive option for promoting soil health and sustainability. In light of these advantages, incorporating biopolymers as promoters represents a promising approach to enhance soil performance while supporting environmentally conscious practices. Among biopolymers, xanthan gums are suggested to be first investigated.

To understand Xanthan Gum's potential as a promoter accurately, comprehensive testing under diverse conditions is essential. Experiments should encompass various soil types, concentrations of Xanthan Gum, and, if possible, comparison with other biopolymers. This thorough approach will yield valuable insights, guiding us in utilizing biopolymeric solutions for improved soil management effectively and sustainably.

CONCLUSION

In conclusion, this paper reviewed conventional and emerging promoters used in gas hydrate formation. Conventional promoters, like SDS and THF, have limitations such as foam formation and high cost. Emerging promoters like Icemax® & Drift® and Amino Acid show promising results in promoting hydrate formation with improved kinetics. As a novel approach, we propose investigating Xanthan Gum, a biopolymer, as a potential promoter for gas hydrate formation due to its properties, such as high specific area, diverse charges, and particle sizes, that could affect the nucleation effect. Biopolymers offer environmental benefits and cost-effectiveness, making them attractive alternatives. Further testing is needed to assess Xanthan Gum's efficacy under different conditions. Embracing innovative promoters can unlock the potential of gas hydrates and foster sustainable energy solutions for the future.

REFERENCE

- Huang, J., Kogbara, R. B., Hariharan, N., Masad, E. A., & Little, D. N. (2021). A State-of-the-Art Review of Polymers Used in Soil Stabilization. *Construction and Building Materials*, 305.
- Kakati, H., Mandal, A., & Laik, S. (2016). Promoting Effect of Al_2O_3/ZnO -Based Nanofluids Stabilized by SDS Surfactant on $CH_4 + C_2H_6 + C_3H_8$ Hydrate Formation. *Journal of Industrial and Engineering Chemistry*, 35, 357-368.

- Kim, N.-J., & Kim, C.-B. (2004). Study on Gas Hydrates for the Solid Transportation of Natural Gas. *KSME International Journal*, 18(4), 699-708.
- Liu, Y.; Chen, B.; Chen, Y.; Zhang, S.; Guo, W.; Cai, Y.; Tan, B.; Wang, W. Methane Storage in a Hydrated Form as Promoted by Leucines for Possible Application to Natural Gas Transportation and Storage. *Energy Technology*, 3, 815–819.
- Nasir, Q., H. Suleman, and Y. A. Elsheikh. (2020). A Review on the Role and Impact of Various Additives as Promoters/Inhibitors for Gas Hydrate Formation. *Journal of Natural Gas Science and Engineering*, 76.
- Sa, J.-H., & Sum, A. K. (2019). Promoting Gas Hydrate Formation with Ice-Nucleating Additives for Hydrate-Based Applications. *Applied Energy*, 251.
- Sowa, B., Zhang, X. H., Hartley, P. G., Dunstan, D. E., Kozielski, K. A., & Maeda, N. (2014). Formation of Ice, Tetrahydrofuran Hydrate, and Methane/Propane Mixed Gas Hydrates in Strong Monovalent Salt Solutions. *Energy & Fuels*, 28(11), 6699-7302.
- Veluswamy, H. P., Hong, Q. W., & Linga, P. (2016). Morphology Study of Methane Hydrate Formation and Dissociation in the Presence of Amino Acid. *Crystal Growth & Design* Volume, 16(10), 5585-6138.
- Yoslim, J., Linga, P., & Englezos, P. (2010). Enhanced Growth of Methane-Propane Clathrate Hydrate Crystals with Sodium Dodecyl Sulfate, Sodium Tetradecyl Sulfate, and Sodium Hexadecyl Sulfate Surfactants. *Journal of Crystal Growth*, 313, 68-80.
- Zhang, J. S., S. Lee, & J. W. Lee. (2007). Kinetics of Methane Hydrate Formation from SDS Solution. *Industrial & Engineering Chemistry Research*, 46(19), 6065–6378.
- Zhang, T., Y.-L. Yang, and S.-Y Liu. (2020). Application of Biomass By-Product Lignin Stabilized Soils as Sustainable Geomaterials: A Review. *Science of Total Environment*, 728.