

Vol. 5, No. 1 (2024); 34-44

Journal of Earth Sciences and Technology

http://www.htpub.org/Journal-Of-Earth-Sciences-And-Technology/



Simulation Based Technique of Methanol and Calcium Chloride Hydrate Inhibitors Injection for Hydrate Formation Prevention

Kingdom Kponanyie Dune^{a*}, Marvin Lezor Kpea-ue^a, Omoni Onimim Dokubo^a

^aDepartment of Petroleum Engineering, Rivers State University, 500101Port Harcourt, Nigeria

Article Information	Abstract
Article History Received: 03/09/2024 Accepted: 25/10/2024 Available online: 09/11/2024	The effective prevention of hydrate formation and ensuring safe and efficient production of deepwater oil and gas resources are technical challenges in the petroleum industry. Combination of thermodynamic inhibitors has been propose to improve the inhibition of hydrate formation and has received significant research attention. However, much has not been done to investigate the promotion of the significant is the provention of the significant comparisities offect of hydrate is hibiters in the provention of the significant comparisities offect of hydrates is hibiters in the provention of the significant comparisities of the significant of the sis the significant of the significant of the sis the significant o
Keywords Methanol Calcium chloride Concentration Hydrate Volume fraction	and combination with calcium chloride (CaCl ₂) on hydrate formation were analyzed. A simulation based method was applied to each volume section of the Pipeline/Riser system and a phase behavior and fluid property program was used to generate input file required by the simulation model. Sensitivity analysis was done for different percentage of inhibitor moles required to suppress hydrate formation for methanol injection and the co-injection of methanol with CaCl ₂ . The result shows that the fluid temperature was above the hydrate formation temperature up to a length of about 9660.54m along the pipeline/riser system and hydrate volume fraction which grows to a maximum value of 0.0000554089 at 12952.7m for the uninhibited system. For the injection of 10mol%, 20mol%, 30mol%, 40mol%, and 50mol% methanol, the hydrate volume fraction grows to a maximum value of 0.0000589137, 0.0000664168, 0.0000422186, 0.0000145381, and 0.000000440159 at 12952.7m, 12952.7m, 13448.5m, 13715.1m, and 13893.4m respectively. Methanol concentration of 60mol% was the optimum concentration required for hydrate prevention. For the co-injection of methanol and CaCl ₂ , 40mol% methanol and 20mol% CaCl ₂ was required for hydrate prevention. The co-injection of methanol and CaCl ₂ results in the reduction of the quantity of methanol required for hydrate prevention by 20%. The co-injection of alcohol and electrolytes should be deployed to reduce the significant quantities of alcohol required for hydrate suppression.

^{*} Corresponding author

E-mail address: Dune.kingdom@ust.edu.ng

This is an open access article under the CC BY licence (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

The effective prevention of hydrate formation and ensuring safe and efficient production and longdistance transportation of deepwater oil and gas resources are key technical challenges in the petroleum industry that require to be addressed urgently (Cao *et al.*, 2020; Xu *et al.*, 2015; Wang *et al.*, 2022a). Preventing hydrate formation is of crucial importance in the natural gas industry. Hydrate inhibitors are chemicals that prevent the formation of hydrates during natural gas extraction, transmission, and processing, which can be categorized into thermodynamic hydrate inhibitors (THIs) and kinetic hydrate inhibitors (KHIs, also named low dosage hydrate inhibitors) (Gulbrandsen and Svartås, 2017). Common thermodynamic hydrate inhibitors (THIs) are electrolytes (NaCl and CaCl₂) and alcohols (methanol, ethylene glycol, and glycerol). The addition of such inhibitors to natural gas streams can alter the chemical sites of an aqueous solution or hydrate phase, thereby shifting the hydrate formation conditions to a lower temperature or higher-pressure range. However, to effectively limit the formation of gas hydrates, the THIs must be injected in significant quantities of which it can cause a number of operational issues and an environmental problem like high costs, toxicity, and an excessive density (Rebolledo-Libreros *et al.*, 2017).

These problems and concerns have spurred on a great interest in KHIs that are able to delay the formation of hydrate. However, the existing KHIs used alone are unable to meet the requirements of the inhibition of methane hydrate in deep-sea exploration activities, where harsh subsea conditions render inhibitors ineffective and favour rapid gas hydrate formation. In recent years, many experimental and theoretical studies have been carried out not only on kinetic and thermodynamic hydrate inhibitors but also reported the effects of thermodynamic and kinetic inhibitor combinations on hydrate inhibition (Zhao *et al.*, 2015; Posteraro *et al.*, 2015). It has been demonstrated in the earlier studies that the performance of a compound system can show a better performance than individual inhibitors (Zhao *et al.*, 2015).

Sa *et al.*, (2011) proved that glycine and L-alanine had a good prospect as thermodynamic inhibitors for CO₂ hydrate formation. Zhao *et al.*, (2015) reported that the compound system of 10 wt.% NaCl and 1.5 wt.% PVP could give a 600 minutes induction time at higher subcooling (16.4°C) and they found out that the performance of poly (vinyl pyrrolidone) was improved when used in combination with thermodynamic hydrate inhibitors. Masoudi and Tohidi, (2010) used a thermodynamic model to study the effects of various salts and thermodynamic inhibitors on hydrate stability zones and concluded that higher concentrations of thermodynamic inhibitors than salts are better for hydrate inhibitor.

A recent study by Kim *et al.*, (2017) presented hydrate formation characteristics in the presence of both MEG (thermodynamic inhibitor) and NaCl (salt). As expected, the hydrate equilibrium conditions were shifted towards low temperature and high-pressure conditions. Although the effect of NaCl on the hydrate onset time and subcooling temperature was negligible, the initial growth rate and the hydrate volume fraction in liquid phase were reduced. Kinate *et al.*, (2023) evaluated the optimum mass percent required to inhibit hydrate formation with deferent hydrate inhibitors singly and concluded that high percentage were required for inhibition, prompting the need for co-injection of electrolytes and alcohol to reduced cost and flexibility.

A combination of thermodynamic and kinetic inhibitors has been proposed to improve the inhibition of hydrate formation and has received significant research attention. However, not much is done to investigate the synergistic effect of hydrate inhibitors. In this work, the inhibition effect of methanol was investigated singly and later co-injected with calcium chloride (an electrolyte).

2. Methodology

2.1 Simulator and Data

Multiflash and OLGA simulator were used with literature data on fluid composition, pipeline geometry, riser geometry, properties of pipeline materials, heat transfer and operating parameters presented in Table 1 to Table 6.

Component Name	Mole %
Nitrogen	0.100
Carbon Dioxide	1.639
Methane	87.346
Ethane	5.747
Propane	2.299
I-Butane	0.480
N-Butane	0.850
I-Pentane	0.260
N-Pentane	0.300
C6	0.280
C7	0.650
C8	0.00011
C9+	0.0005
Water	0.05

Table 1. Fluid composition (Okereke et al., 2019)

C9+ Density = 0.8 g/cc

C9+ Molecular weight = 300kg/kmol.

X-Coordinate (m)	Y-Coordinate (m)	Diameter (in)	Roughness (in)
0	-989	7	0.0006
1300	-985	7	0.0006
4100	-995	7	0.0006
4900	-1000	7	0.0006
6400	-985	7	0.0006
6800	-980	7	0.0006
7200	-975	7	0.0006
7900	-970	7	0.0006
8700	-965	7	0.0006
9600	-960	7	0.0006
10200	-955	7	0.0006
11200	-950	7	0.0006
12900	-945	7	0.0006

Table 2. Pipeline geometry (Okereke et al., 2019)

Table 3. Riser geometry (Okereke et al., 2019)

X-Coordinate (m)	Y-Coordinate (m)	Diameter (in)	Roughness (in)
12900	-945	7	0.0006
12970	-600	7	0.0006
13002	-100	7	0.0006
13005	0	7	0.0006
13006	40	7	0.0006

Table 4. Properties of the pipeline materials (Nemoto, et al., 2010)

Material	Density (kg/m ³)	Specific heat (J/kg K)	Thermal conductivity (W/m K)	Wall thickness (mm)
Steel	7850	500	50	8
Insulation	1000	1500	0.135	13.28

Table 5. Heat transfer data

Property	Value
Pipeline overall heat transfer coefficient	8W/m ² -C
Riser overall heat transfer coefficient	8W/m ² -C
Riser and pipeline ambient temperature	4-20°C

Table 6: Operating parameters

Property	Value
Inlet mass flow rate	15kg/s
Inlet temperature	60°C
Outlet temperature	22°C
Outlet pressure	27psig

2.2 Simulation Approach

Multiflash, a phase behavior and fluid property program was used to generate input file required by OLGA model. A based model without inhibitors addition was built and later a case with only methanol as the injected inhibitor and then the co-injection of methanol and calcium chloride (CaCl₂). Data in Table 1 was encountered for the gas composition as a feed into Multiflash package for the generation of hydrate and PVT files. An OLGA case was created and the flow path together with the nodes representing the inlet and outlet of the system were added. The system consisted of a closed node at the beginning of the pipeline with a mass source at the inlet, a flow path representing the pipeline/riser and a pressure node operating at 50psig and 10°C at the outlet. The pipeline/riser materials and geometry data presented in Table 2, Table 3, and Table 4 were used to define the pipeline/riser system. Data in Table 5 were used in defining the environment and heat transfer between the system and its surroundings. The CSMHyK model was selected as the hydrate model with structure II hydrate as the hydrate phase. The heat transfer from the pipeline wall to the surroundings and a mass source rate of 15kg/s were defined the heat transfer and source keys respectively. The model was run for a total time of 2hrs. The simulation workflow for this study is shown in Figure 1.

3. Results and Discussion

3.1 Hydrate formation possibilities in uninhibited system

The fluid pressure and temperature hydrate volume fraction and the difference between hydrate and section temperature is presented in figure 2. A positive value of 6.22524°F for the difference between hydrate and section temperature was observed at about 9660.54m which implies the formation of hydrate. The fluid temperature was above the hydrate formation temperature up to a length of about 9660.54m along the pipeline/riser system. Beyond this length, the prevailing conditions of temperature and pressure (571.04psia and 49.4653°F) was within the hydrate formation zone and hydrate formed with initial volume fraction of 0.00000803015 at 9660.54m which grows to a maximum value of 0.0000554089 at 12952.7m.



Fig. 1. Simulation workflow.



Fig. 2. Section and hydrate variables for uninhibited system (base case).

3.2 Injection of 10mol% methanol

The fluid pressure and temperature, hydrate volume fraction and the difference between hydrate and section temperature for injection of 10 mol% of methanol is shown in Figure 3. Result shows a negative difference between hydrate and section temperature up to about 10156.3m along the pipeline where the operating conditions of the system were completely out of the hydrate zone. Beyond this point, the difference between hydrate and section temperature was positive which implies the prevailing conditions of temperature and pressure (538.185psia and 46.8918°F) was within the hydrate envelope. The hydrate volume fraction grows to a maximum value of 0.0000589137 at 12952.7m. A decrease in temperature and pressure gradually increases the hydrate volume fraction and align with the study of Kinate et al. (2023).



Fig. 3. Section and hydrate variables for 10mol% methanol.

3.3 Injection of 20mol% methanol

Figure 4 shows hydrate (volume fraction and the difference between hydrate and section temperature) and fluid (pressure and temperature) for 20mol% of methanol injected in to the system. There was a negative difference between hydrate and section temperature up to a length of about 10969.8m where the system operated outside the hydrate zone. Downstream of the line, the difference between section and hydrate formation temperature (6.49503°F) was positive at the prevailing conditions of pressure and temperature (481.469psia and 42.4115°F). The hydrate volume fraction grows to a maximum value of 0.0000664168 at 12952.7m.

3.4 Injection of 30mol% methanol

The effect of injection of 30mol% of methanol on hydrate inhibition in the system is presented in figure 5. There was a negative difference between hydrate and section temperature along the system up to about 9660.54m. Beyond 9660.54m, the difference between hydrate and section temperature was positive with a value of 6.22524°F, which implies the formation of gas hydrate downstream of the system from 9660.54m. Hydrate was form with an initial volume fraction of 0.000000273298 which grow to a maximum value of 0.0000422186 at about 13448.5m.



Fig. 4. Section and hydrate variables for 20mol% methanol.



Fig. 5. Section and hydrate variables for 30mol% methanol.

3.5 Injection of 40mol% methanol

Figure 6 shows the effects of injection of 40mol% of methanol on hydrate formation inhibition. Result shows that the addition of 40mol% of methanol reduces gas hydrate formation in the system. The system operating parameters (pressure and temperature) were above the hydrate formation temperature to about 13041.7m. Downstream of the line, there was an initial volume fraction of 0.000000343114 at 13041.7m which grow to a maximum value of 0.0000145381 at about 13715.1m.



Fig. 6. Section and hydrate variables for 40mol% methanol.

3.6 Injection of 50mol% methanol

The effects of injecting 50 mol% methanol on the inhibition of hydrate formation is depicted in Figure 7. 50 mol% methanol injections further lessen the possibility of gas hydrate formation in the system. There was a negative difference between hydrate and section temperature up to about 13791.7m which implies operation outside the hydrate zone and the absent of hydrate phase in the system. Downstream of the line shows an initial volume fraction of 0.0000000418856 at 13791.7m which grow to a maximum value of 0.000000440159 at about 13893.4m. At 50 % mol concentration methanol injection, there was a minimum hydrate formation tendency along the pipeline.



Fig. 7. Section and hydrate variables for 50mol% methanol.

3.7 Injection of 60mol% methanol

Figure 8 shows the effects of injection of 60 mol% methanol on hydrate formation on the system. Result shows that at all conditions of temperature and pressures, the injection of 60 mol% methanol inhibit the system from hydrate formation. This was zero-hydrate volume fraction and the negative value of the difference between hydrates and section temperature throughout the system. Also, at decrease in temperature and pressure conditions along the pipeline, there was no hydrate formation giving 60% as the

optimum mass percent of methanol to inhibit hydrate formation which agreed with the study of Kinate et al. (2023).



Fig. 8. Section and hydrate variables for 60 mol% methanol.

3.8 Co-injection of Methanol and CaCl₂

The section and hydrate variables for the co-injection of 40 mol% methanol and 20 mol% $CaCl_2$ are shown in figure 9. The difference between hydrate and section temperature was negative throughout the entire system and no hydrate was form. In comparison to the case with the injection of 60 mol% methanol which completely inhibits the system from hydrate formation, the result obtained reveals that the amount of methanol required was reduced by 20 mol%. Increasing the mol % of CaCl2 and reducing the methanol inhibits hydrate formation with a decrease in temperature and pressure.



Fig. 9. Section and hydrate variables for 40 mol% methanol and 20 mol% CaCl₂.

4. Conclusion

In this work, a simulation-based approach of hydrate formation inhibition with methanol and calcium chloride were investigated. The impact of the injection of methanol and methanol with CaCl₂ were

assessed using the volume fraction of hydrate form in the pipeline. Sensitivity analysis was done for the percentage of inhibitor required to suppress hydrate form both for the Injection of methanol and the co-injection of methanol and CaCl₂. The following conclusions were drawn from the study:

- i. A higher concentration of methanol was required for hydrate suppression in the system when it was the only inhibitor in the system.
- ii. The co-injection of methanol and $CaCl_2$ results in the reduction of the quantity of methanol required for hydrate prevention by 20%.
- iii. A methanol concentration of 60mol% was the optimum concentration required for hydrate prevention.
- iv. With the co-injection of methanol and CaCl₂, 40mol% methanol and 20mol% CaCl₂ was required for hydrate prevention.

References

- Cao, Q., Xu, D., Xu, H., Luo, S., and Guo, R. (2020). Efficient promotion of methane hydrate formation and elimination of foam generation using fluorinated surfactants. *Frontiers in Energy*, 14, 443–451.
- Gulbrandsen, A. C., and Svartås, T. M. (2017). Effects of PVCap on Gas Hydrate Dissociation Kinetics and the Thermodynamic Stability of the Hydrates. *Energy Fuels*, 31, 9863–9873.
- Kim, H., Park, J., Seo, Y., and Ko, M. (2017). Hydrate risk management with aqueous ethylene glycol and electrolyte solutions in thermodynamically under-inhibition condition. *Chemical Engineering Science*, 158, 172.
- Kinate, B. B., Igwe, I., and Elikee, U. D. (2023). Prediction of Optimum Hydrate Inhibitors Mass Percent for Hydrate Formation Prevention. *Journal of Earth Energy Science, Engineering and Technology*, 6(3);81-94.
- Masoudi, R., and Tohidi, B. (2010). On modelling gas hydrate inhibition by salts and organic inhibitors. *Journal of Petroleum Science and Engineering*, 74(3), 132.
- Nemoto, R. H., Baliño, J. L., Tanaka, R. L., and Godinho, C. A. (2010). A case study in flow assurance of a pipeline-riser system using OLGA. 13th Brazilian Congress of Thermal Sciences and Engineering December 05-10, Uberlândia, MG, Brazil.
- Okereke, N. U., Edet, P. E., Baba, Y. D., Izuwa, N. C., Kanshio, S., Nwogu, N., and Nwanwe, O. (2019). An assessment of hydrates inhibition in deepwater production systems using low-dosage hydrate inhibitor and monoethylene glycol. *Journal of Petroleum Exploration and Production Technology*, 10, 1169–1182.
- Posteraro, D., Ivall, J., Maríc, M., and Servio, P. D. (2015). New insights into the effect of polyvinylpyrrolidone (PVP) concentration on methane hydrate growth. 2. Liquid phase methane mole fraction. *Chemical Engineering Science*, 126, 91–98.
- Rebolledo-Libreros, M. E., Reza, J., Trejo, A., and Guzmán-Lucero, D. J. (2017). Evaluation of copolymers from 1-vinyl-3alkylimidazolium bromide and N -vinylcaprolactam as inhibitors of clathrate hydrate formation. *Journal of Natural Gas Science and Engineering*, 40, 114–125.
- Sa, J. H., Lee, B. R., Park, D. H., Han, K., Chun, H. D., and Lee, K. H. (2011). Amino acids as natural inhibitors for hydrate formation in CO2 sequestration. *Environmental Science and Technology*, 45, 5885–91.
- Wang, J., Sun, J., Wang, R., Lv, K., Wang, J., Liao, B., Shi, X., Wang, Q., Qu, Y., and Huang, H. (2022a). Mechanisms of synergistic inhibition of hydrophilic amino acids with kinetic inhibitors on hydrate formation. *Fuel*, 124012
- Xu, S., Fan, S., Wang, Y., and Lang, X. (2015). An Investigation of Kinetic Hydrate Inhibitors on the Natural Gas from the South China Sea. Journal of Chemical and Engineering Data, 60, 311–318.
- Zhao, X., Qiu, Z., Zhou, G., and Huang, W. (2015). Synergism of thermodynamic hydrate inhibitors on the performance of poly (vinyl pyrrolidone) in deepwater drilling fluid. *Journal of Natural Gas Science and Engineering*, 23, 47–54.