



Comparative Analysis of Gas Hydrate Chemical Inhibitors

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ABSTRACT

Natural gas hydrate formation prevention by injection of chemical inhibitors of different weight percentages was investigated. The chemical inhibitors investigated in this study are methanol, ethylene glycol, diethylene glycol and triethylene glycol of different weight percentages of 10%, 20%, 25% and 40%. Natural gas hydrate formation was mitigated against by these chemical inhibitors by reducing hydrate formation temperature due to its high value of depression temperature. Methanol gives the least hydrate formation temperature among the chemical inhibitors with a deviation of 95% compare with hydrate formation temperature without inhibitor.

Keywords: Hydrate formation temperature, chemical inhibitors weight percent, temperature depression, Nielsen-Bucklin equation, Peng-Robinson equation

INTRODUCTION

Natural gas hydrates refer to ice-like structures in which methane is trapped inside of water molecules. Gas hydrates are found under arctic permafrost, beneath the ocean floor and formed during well drilling and production processes. Therefore, gas hydrates have led to more difficulties or constraints than solutions as its formation in deep-water production causes production and processing operations constraints, thus controlling or mitigating gas hydrate formation in deep-water oil and gas wells and pipelines is a challenge and resolving the existence of gas hydrates is a major part of planning for deep-water drilling and production. However, with respect to deep water drilling, gas hydrates can act as a source of natural gas as 164 cubic feet of natural gas is released from one cubic foot of gas hydrate [1]. Hence, the amount of gas within the world's gas hydrate accumulations is estimated to greatly exceed the volume of all known conventional gas resources [2].

The composition of gas hydrates includes water, methane, ethane, propane, isobutane, normal butane, carbon dioxide, nitrogen, hydrogen sulphide and is polyhedral crystalline solids structure of hydrogen bonded water molecule, also called clathrate. The polyhedral molecule results in cages that consist at most one of guest(gas) molecule each. Vander Waals forces exist between the water(host) molecule and the enclathrated guest(gas) molecule that formed the cages and under extreme condition, two guest molecules be in the same cage [3]. Natural gas hydrates consist of low quantity of gas molecules contained in a mesh cage system consisting mainly of water molecules. When hydrate constituents are in contact at high pressure and low temperature conditions, solid structures of different crystals of higher densities than typical fluid hydrocarbon are formed [4]. Hydrate structure consist of cavities that are formed by hydrogen bond of cluster of cyclic water. This closed ring structure is more stable than the linear cluster due to hydrogen bond [5].

Nucleation and growth are the two main mechanisms of gas hydrate formation. The nucleation could be defined as a process where gas-water cluster(nuclei) grow and are dispersed until it reaches to critical size. This could be homogenous when it occurs spontaneously or heterogeneous when it is induced around impurities. Primary nucleation starts without crystal being present while secondary nucleation starts where crystal have grown already. Induction time is a time the first gas-liquid contact to the first detection of hydrate phase. The induction time was used to predict the nucleation period and it states that, induction time increases dramatically when the driving force for hydrate formation approaches zero [6].

Flow assurance is characterized with risks and difficulties due to the nature and characteristics of produce hydrocarbons associated fluids and solids. The structured engineering analysis process enables the application of the fluid properties and thermal hydraulic analysis of the system to unfold control strategies for hydrate, wax, asphaltenes and scale [7]. The process of hydrate formation is influenced by three factors:

1. Kinetics of crystal growth at the surface.
2. Mass transfer component to the growing surface.
3. Heat transfer component away from the growing surface.

During growth operation, pressure and temperature are reduced linearly and thus, gas reacts with water and no hydrate is formed and this is known as induction time. This refers to the period of hydrate forming process and its onset. One of the main difficulties associated with upstream and downstream sector of oil and gas industry today is the prevention of natural gas hydrate constraints such as pipeline blockage, separation facilities and instruments blockage, pressure and flow monitoring errors, reduction in the volume of natural gas transported, increase in pipeline pressure differences and thus, damaging the pipe fittings [8].

Hydrate formation prevention by anti-agglomerate technique prevents the deposition or converging of hydrate by forming a hydrate sherry comprises of liquid hydrocarbon and transported through pipeline [9]. The effect of hydrate formation prevention by ethylene glycol was considered by using field operating conditions before and after its application. Output production increment from 75.073MMBtu/day to about 127.827MMBtu/day, representing 41.2% of the initial gas production of the field after ethylene glycol injection into the production zone. Hence, ethylene glycol acted as an inhibitor by removing hydrate plug from pipe thereby increasing production output [10].

This investigation dealt with the formation of gas hydrate, its effects on production, operation and processing in oil and gas industry, future projection of natural gas production from gas hydrates and natural gas hydrate preventions by the application or injection of chemical inhibitors in a gas field in Niger Delta region of Nigeria. The technique of gas gravity is applied in quantifying hydrate formation condition and determining hydrate formation temperature. This study simulation is performed by using Peng-Robinson equation of state embedded in Aspen Hysys software and the initial simulation is carried out with no chemical inhibitor, while further simulations involve injection of inhibitors such as methanol, ethylene glycol, diethylene glycol and triethylene glycol of different weight percentages 10%, 20%, 25% and 40% respectively. The results of these simulations are compared and their effects are examined, analysed and inference made.

METHODOLOGY

The compositions of gas field investigated in this study is deduced from a gas well located in the Niger Delta region of Nigeria. The gas field stream of the gas well and the quantity of chemical inhibitors injected in these analysis is shown in table -2. The chemical inhibitors are characterized and its operating conditions and other physical parameter are highlighted thus.

Gas Gravity

The gas gravity refers to the ratio of molecular weight of the gas to that of air. This technique is helpful when the composition of gas is unknown and in deducing hydrate formation condition for mixture of sweet gas.

$$SG = \sum_{i=1}^n \frac{y_i M_{wi}}{M_{wair}}$$

Temperature Depression

The total quantity of inhibitor such as methanol, ethylene glycol, diethylene glycol and triethylene glycol injected into the zone to prevent hydrate formation is expressed by temperature depression. The percentage in mole of chemical inhibitor in the produced water influences the hydrate formation temperature. The amount of inhibitors in aqueous liquid hydrocarbon, vapour and liquid hydrocarbon is the required quantity for inhibiting hydrate formation.

Hammer-Schmidt equation is applied in determining the concentration of inhibitor in the aqueous phases with the assumptions that inhibitor effect is independent of pressure, temperature of depression is independent of the nature of hydrate former present and the type of hydrate formed. The Hammer-Schmidt equation is applicable for natural gases with methanol concentrations 20-25wt% and 60-70wt% for glycol and the expression is shown below:

$$\Delta T = \frac{kw}{100(mw)-(mw)w}$$

Nielsen- Bucklin Equation

Considering methanol concentration of about 25-50wt%, Nielson- Bucklin equation is established to estimate the concentration of inhibitor in the final water phase. The Nielsen-Bucklin equation is expressed as:

$$\Delta T = -72 \ln(1 - x)$$

The expression for predicting the weight percent of inhibitor in the final water phase was deduced from mathematical analysis and expression of Nielsen-Bucklin equation as:

$$x_m = 1 - e^{-\frac{\Delta T}{72}}$$

Table -1 Field Composition

Components	CH ₄	C ₂ H ₆	C ₃ H ₈	i-C ₄ H ₁₀	C ₄ H ₁₀	i-C ₅ H ₁₂	C ₅ H ₁₂	C ₆ H ₁₄₊	CO ₂	N ₂	Total
Mole Fraction(%)	95.17	2.66	0.58	0.16	0.17	0.09	0.07	0.03	0.937	0.13	100.00
Molecular Weight	16	30.1	44.1	58.1	58.1	72.2	72.2	86	44	28	508.8
Average Molecular Weight (Y _i M _i)	15.2272	0.8007	0.2558	0.0930	0.0988	0.0650	0.0505	0.0258	0.4122	0.0364	117.065

Table -2 Gas Field Stream and Inhibitor Weight Percent

Inhibitor(Wt%)	10,20,25,40
Temperature (°C)	16.9828
Pressure (bar)	17.2369
Flow Rate (m ³ /h)	54.66036
Free Water Rate (barrel/day)	6.58
Comp Mole Frac (Methane)	0.948301
Comp Mole Frac (Ethane)	0.032284
Comp Mole Frac (Propane)	0.001594
Comp Mole Frac (i-Butane)	0.001694
Comp Mole Frac (n-Butane)	0.000897
Comp Mole Frac (i-Pentane)	0.000697
Comp Mole Frac (n-Hexane)	0.000299
Comp Mole Frac (CO ₂)	0.009337
Comp Mole Frac (Nitrogen)	0.001295
Comp Mole Frac (H ₂ O)	0.003602
Hydrate Formation Temp (C)	1.095
Hydrate Formation Pressure (bar)	104.180

Table -3 Inhibitors Input Parameters

Inhibitor	M	X _m	K	W
MEOH	32	0.612	233	0.02303
EGLYCOL	62.07	0.642	270	0.01386
DEGLY-	106.1	0.723	400	0.00884
TEGLY-	150.1	0.763	540	0.00642

Table -4 Inhibitors Operating Conditions

Inhibitor Type	Methanol	EGlycol	DEGLycol	TEGLycol
Formation temperature after injection	-1.4865	-0.3565	-1.6415	1.0899
Operational Temp Gain	2.5815	1.4515	2.7365	0.0051
Formation pressure after Injection	130.32	126.82	152.51	140.97
Operational Pressure Gain	26.14	22.64	48.33	36.79

Table -5 Chemical Inhibitor Temperature Depression Values

Reagent	10% wt	20% wt	25% wt	40% wt
MeoH	8.107639	18.24219	24.32292	48.64583
MEG	4.833253	10.87482	14.49976	28.99952
DEG	4.188131	9.423294	12.56439	25.12879
TEG	3.995472	8.989812	11.98642	23.97283

Table -6 Hydrate Formation Temperature

Pressure (Psia)	Hydrate Formation Temperature @ SG=0.56 (°F)
3000	73.2331
2800	72.3324
2600	71.3649
2400	70.32
2200	69.1841
2000	67.9398
1800	66.5643
1600	65.0266
1400	63.2834
1200	61.271
1000	58.8907
800	55.9776
600	52.2219
400	46.9286
200	37.8795

Hydrate Formation Temperature

The Katz plot curve fit equation is used to deduce hydrate formation temperature at specific gas gravity. Gas gravity of 0.56 was estimated and applied in this investigative study. The Katz plot equation is expressed thus [11]:

$$T = 13.055 \ln(P) - 31.29$$

Simulation Model

The three phase hydrate prediction was carried out by combining Peng-Robinson equation of state with Hysys simulator. The simulator parameters such as pressure, composition of natural gas, inhibitors and water content are specified and initiated in the simulator. The first simulation is carried out with no inhibitor and the resulting output analysed. In addition, simulation of hydrate formation temperature with the introduction of chemical inhibitors such as methanol, ethylene glycol, diethylene glycol and triethylene glycol of different weight percent of 10wt%, 20wt%, 25wt% and 40wt% respectively were investigated. The resulting hydrate temperature formation is then analysed and compare with hydrate temperature formation of no chemical inhibitor. The Peng-Robinson equation of state is expressed below.

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

$$a = \frac{0.45724R^2T_c^2}{P_c}$$

$$b = \frac{0.07780RT_c}{P_c}$$

$$\alpha = (1 + (1 - T_r^{0.5}))^2$$

$$K = 0.37464 + 1.54226w - 0.26992w^2$$

$$T = T_r T_c$$

RESULTS

Effective Temperature Depression

The temperature depression value of each chemical inhibitor at different weight percentage was determined and the result tabulated below.

Hydrate Formation Temperature

The hydrate formation temperature of the gas field was determined at varying operating pressure at gas gravity of 0.56 by using Katz plot equation stated above. The hydrate formation temperature with no chemical inhibitor was calculated first and the resulting temperature values expressed in degree Fahrenheit. The gas field pressure temperature curve is plotted at no inhibitor injection.

In addition, similar algebraic calculations were performed on the gas field after the injections of chemical inhibitors methanol, ethylene glycol, diethylene glycol and triethylene glycol of different weight percentages of 10% wt, 20% wt, 25% wt and 40% wt respectively. The resulting outputs are tabulated for each chemical inhibitor and the pressure-temperature curves at each weight percentage are shown below.

Table -7 Effective Temperature Depression for Methanol and Ethylene Glycol(°F)

Methanol				Ethylene Glycol			
10% wt	20% wt	25% wt	40% wt	10% wt	20% wt	25% wt	40% wt
65.125	54.991	48.91	22.043	68.4	62.358	58.733	44.234
64.225	54.09	48.009	21.143	67.499	61.458	57.833	43.333
63.257	53.123	47.042	20.175	66.532	60.49	56.865	42.365
62.212	52.078	45.997	19.13	65.487	59.445	55.82	41.32
61.076	50.942	44.861	17.994	64.351	58.309	54.684	40.185
59.832	49.698	43.617	16.75	63.107	57.065	53.44	38.94
58.457	48.322	42.241	15.374	61.731	55.689	52.065	37.565
56.919	46.784	40.704	13.837	60.193	54.152	50.527	36.027
55.176	45.041	38.96	12.094	58.45	52.409	48.784	34.284
53.163	43.029	36.948	10.081	56.438	50.396	46.771	32.271
50.783	40.649	34.568	7.701	54.057	48.016	44.391	29.891
47.87	37.735	31.655	4.788	51.144	45.103	41.478	26.978
44.114	33.98	27.899	1.032	47.389	41.347	37.722	23.222
38.821	28.686	22.606	-	42.095	36.054	32.429	-
29.772	19.637	13.557	-	33.046	27.005	23.38	-

Table 8 Effective Temperature Depression for Diethylene Glycol and Triethylene Glycol(°F)

Diethylene Glycol				Triethylene Glycol			
10% wt	20% wt	25% wt	40% wt	10% wt	20% wt	25% wt	40% wt
69.045	63.81	60.669	48.104	69.238	64.243	61.247	49.26
68.144	62.909	59.768	47.204	68.337	63.343	60.346	48.36
67.177	61.942	58.801	46.236	67.369	62.375	59.378	47.392
66.132	60.897	57.756	45.191	66.325	61.33	58.334	46.347
64.996	59.761	56.62	44.055	65.189	60.194	57.198	45.211
63.752	58.517	55.375	42.811	63.944	58.95	55.953	43.967
62.376	57.141	54	41.436	62.569	57.574	54.578	42.591
60.838	55.603	52.462	39.898	61.031	56.037	53.04	41.054
59.095	53.86	50.719	38.155	59.288	54.294	51.297	39.311
57.083	51.848	48.707	36.142	57.276	52.281	49.285	37.298
54.703	49.467	46.326	33.762	54.895	49.901	46.904	34.918
51.789	46.554	43.413	30.849	51.982	46.988	43.991	32.005
48.034	42.799	39.658	27.093	48.226	43.232	40.235	28.249
42.74	37.505	34.364	-	42.933	37.939	34.942	-
33.691	28.456	25.315	-	33.884	28.89	25.893	-

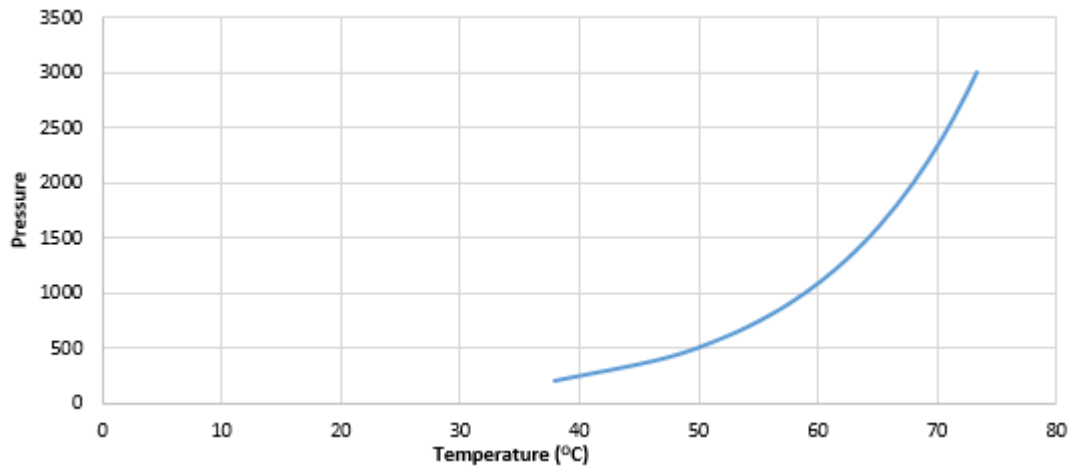


Fig .1 Hydrate Formation Temperature Curve with No Inhibitors

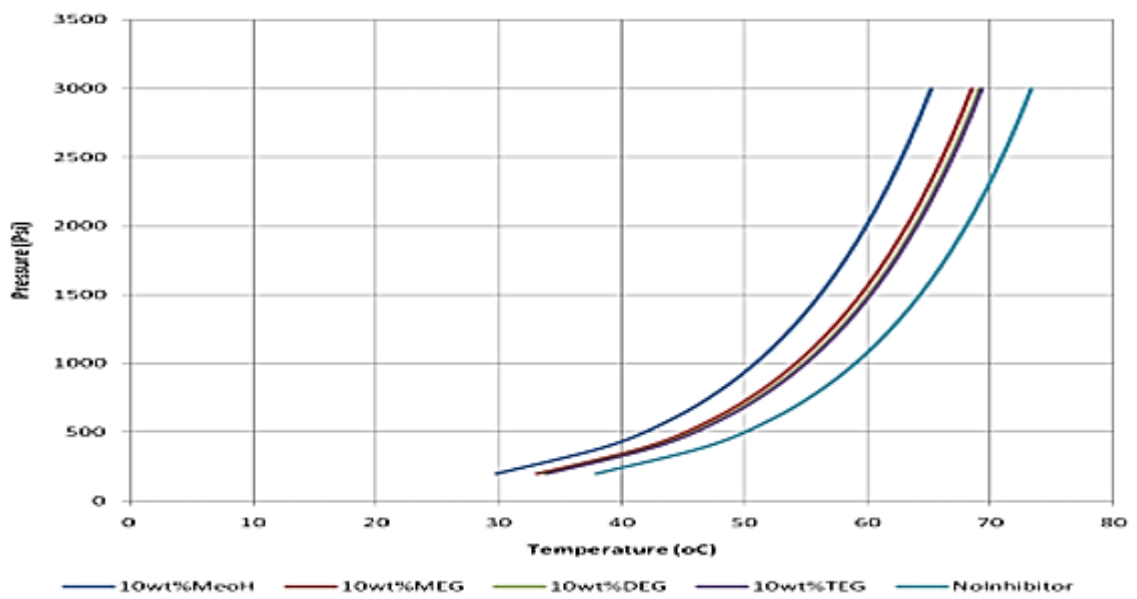


Fig. 2 Hydrate Formation Temperature Curves at no Inhibitor and 10%wt of chemical inhibitors

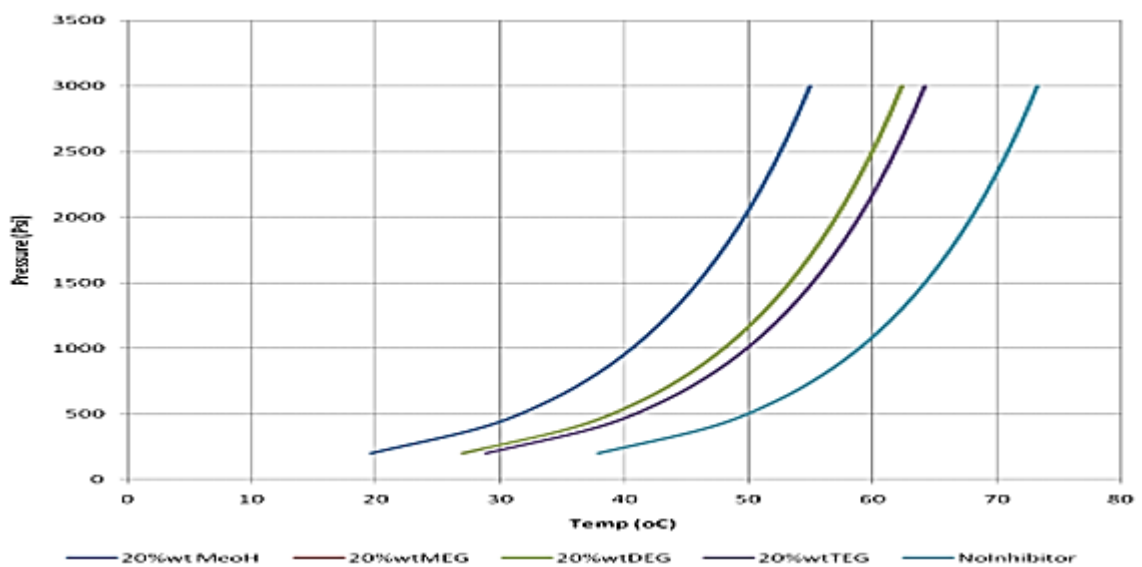


Fig. 3 Hydrate Formation Temperature Curves at no Inhibitor and 20%wt of Chemical Inhibitors

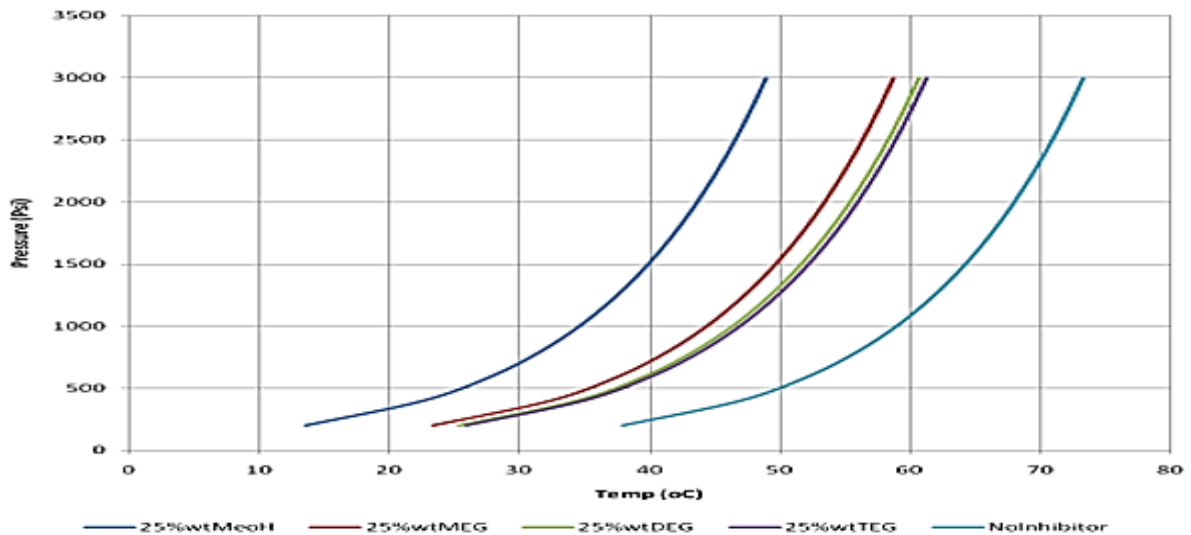


Fig. 4 Hydrate Formation Temperature Curves at no Inhibitor and 25%wt of chemical inhibitors

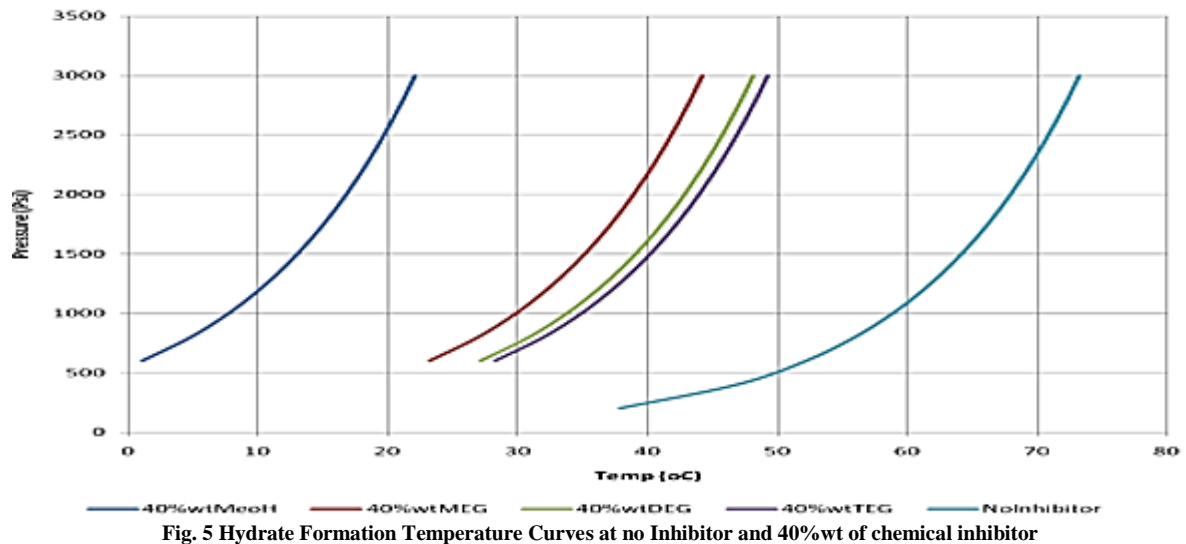


Fig. 5 Hydrate Formation Temperature Curves at no Inhibitor and 40%wt of chemical inhibitor

DISCUSSION

The effective temperature depression table shows that methanol has the higher temperature depression value at any specified weight percent as compared with ethylene glycol, diethylene glycol and triethylene glycol. Hence, increase in the quantity or amount of chemical inhibitors weight percent injected, increases the temperature depression value, thereby reducing hydrate formation temperature at any specified pressure value.

The hydrate formation temperature curve shown in Figure 1 slopes downward from right to left such that at high pressure, hydrate formation temperature is relatively high and low at low pressure. The introduction of chemical inhibitors, methanol, ethylene glycol, diethylene glycol and triethylene glycol as shown in Figures 2-5 yields substantive reduction in hydrate formation temperature for different chemical inhibitor's weight percentages. Methanol inhibitor is the most effective and efficient chemical inhibitor among the inhibitors on the basis of its reduction trend in hydrate formation temperature as its weight percentage increases from 10% wt to 40% wt.

CONCLUSION

Hydrate formation prevention is of utmost importance in oil and gas industry. Its prevention by chemical method that involves injection of chemical inhibitors methanol, ethylene glycol, diethylene glycol and triethylene glycol is also prominent. Thus, this investigative study analyses different chemical inhibitors of different weight percentages. It can be deduced that at different weight percentages of 10% wt, 20% wt, 25% w and 40% wt, the effective trends of different chemical inhibitors at the same weight percentages were examined and plotted. Methanol shows the high-

est temperature depression values, thereby reducing hydrate formation temperature to the minimum among other inhibitors (ethylene glycol, diethylene glycol and triethylene glycol).

Nomenclature

MeOH: Methanol	M_{wair} : Molecular weight of air	CH ₄ : Methane
MEG: Monoethylene glycol	P: Pressure	C ₂ H ₆ : Ethane
DEG: Diethylene glycol	T: Temperature	C ₃ H ₈ : Propane
TEG: Triethylene glycol	T_r : Reduced temperature	i-C ₄ H ₁₀ : Isobutane
SG: Specific gravity	T_c : Critical temperature	C ₄ H ₁₀ : Butane
Y_i : Mole fraction of component i	P_c : Critical Pressure	i-C ₅ H ₁₂ : Isopentane
M_w : Molecular weight	V_c : Critical molar volume	C ₅ H ₁₂ : Pentane
ΔT : Temperature of depression	V_m : Molar volume	C ₆ H ₁₄₊ : Hexane plus
M: Molecular weight of inhibitor	Z: Compressibility factor	CO ₂ : Carbondioxide
C: Physical constants of inhibitor	ω : Acentric factor	N ₂ : Nitrogen gas
W: Weight percent of inhibitor		

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