Chemical Control of Natural Gas Hydrate

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Abstract— The study investigates chemical control of hydrates in pipeline by the application of different chemical substances such as methanol, ethylene glycol, diethylene glycol and triethylene glycol. Aspen Hysys simulator was used to determine hydrate formation temperature based on gas field composition and operating pressure by using Peng-Robinson equation. Similar simulations were carried out with the injection of chemical inhibitors such as methanol, ethylene glycol, diethylene glycol and triethylene glycol. The chemical inhibitors prevent hydrate formation by increasing depression temperature thereby reducing hydrate formation temperature, and thus mitigating against hydrate formation and ensuring constant flow and production of fluid with methanol been the most effective chemical inhibitor based on the hydrate formation temperature reduction trends and analysis.

Index Terms— Hydrate formation temperature; chemical inhibitors; gas gravity; temperature depression; Aspen Hysys simulator.

I. INTRODUCTION

Gas hydrates composed of water, methane, ethane, propane, isobutene, normal butane, carbondioxide, nitrogen, hydrogensulphide and are crystalline solids also called clathrate. Its structure is polyhedral of hydrogen bonded water molecule. The polyhedral structure form cages that contain at most one of guest(gas) molecule each. The cages are held by an intermolecular force (Vander Waals) between the water(host) molecule and the enclathrated guest(gas) molecule. It is noted that in extreme condition, two guest molecules may enter the same cage [1]. Natural gas hydrates are nonstoichiometric solid substances that are captured in a mesh cage system made up of water molecules and contains low amount of gas molecules. At high pressure and low temperature condition, when hydrate constituents are in contact and coagulate, a solid substance of different crystal structures that possesses high densities than typical fluid hydrocarbons emerge [2]. The hydrate structure is composed of cavities which are formed by hydrogen bond of cluster of cyclic water. The closed ring structure attains stability than the linear cluster as a result of the extra bond of hydrogen [3].

The mechanism of gas hydrate formation is mainly based on two phenomena, the nucleation and growth which have the same process like that of precipitation of salt from solution. The nucleation could be termed as a microscopic phenomenon where gas-water cluster(nuclei) grow and are dispersed until it grows 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 [4].

Flow assurance has to do with the risks and problems arising from the challenging properties and behavior of produce hydrocarbons associated fluids and solids. The structured engineering analysis process ensures the utility of the in-depth knowledge of the properties of fluid and thermal hydraulic analysis of the system to develop control strategies for hydrate, wax, asphaltenes and scale [5]. Hydrate growth process is considered to be a combination of three elements; the kinetics of crystal growth at the surface of hydrate, mass transfer component to the growing surface and the heat transfer component away from the growing surface. In growth process, gas reacts with water after the pressure and temperature have being reduced linearly, hence at this stage no hydrate is formed and it is termed induction time. The induction time is understood to be a period of entering to a hydrate forming region and the onset of hydrate formation. Natural gas hydrate is one of the main issues facing the petroleum and gas industry today since its effect have been felt worldwide in the upstream and downstream sector. The associated constraints with natural gas hydrate include blockage of pipeline, blockage of separation facilities and instruments, pressure and flow monitoring errors, reduction in the volume of natural gas transported, increase in pipeline pressure differences and thus damaging the pipe fittings.

Anti-agglomerate method of hydrate control prevents the hydrate from depositing or agglomerating by forming a hydrate sherry which is transported through pipeline and comprise mainly of liquid hydrocarbon [6]. The effect of ethylene-glycol on hydrate formation process was analyzed by considering operating condition of the field before and after injection of glycol. There is increased production from 75.073MMBtu/day to about 127.827MMBtu/day, which is 41.2% of the initial gas production of the field after injecting the field with low dosage ethylene glycol into the production zone. It can therefore be deduced that ethylene glycol acted as an inhibitor since it helps in dissociating hydrate plug from pipe which amounted to increase in production [7].

This study investigates hydrate formation temperature and its inhibition by chemical technique on a gas field in Niger Delta region of Nigeria. Gas gravity approach is used as a result of its effectiveness in quantifying hydrate formation condition for mixture of sweet gas and in determining hydrate formation temperature. The amount of chemical inhibitors required for hydrate formation prevention is estimated by using temperature depression method based on

the associated assumptions. The application of Aspen Hysys as a useful simulator for hydrate formation temperature and prevention analysis by applying methanol, ethylene glycol, diethylene glycol and triethylene glycol as inhibitors. The

effects of these inhibitors on hydrate formation temperature are examined, compared and deductions are made.

TABLE I: 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)	15.22	0.8007	0.2558	0.0930	0.0988	0.0650	0.0505	0.0258	0.4122	0.0364	117.065

TABLE II: GAS FIELD STREAM CONDITION

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 (N ₂)	0.001295
Comp Mole Frac (H ₂ O)	0.003602
Hydrate Formation Temp (°C)	1.095
Hydrate Formation Pressure (Bar)	104.180

TABLE III: INHIBITORS INPUT PARAMETERS

INHIBITOR	M	X _m	C	W
MEOH	32	0.612	2335	0.02303
EGLYCOL	62.07	0.6423	2700	0.013869
DEGLYCOL	106.12	0.7231	4000	0.008848
TEGLYCOL	150.17	0.7634	5400	0.00642

II. METHODOLOGY

The compositions of gas field A in the Niger Delta region of Nigeria applicable in this study are shown below.

A. Gas Gravity

The gas gravity is defined as the ratio of molecular weight of the gas to that of air. This method is best applicable when gas composition is not known and is useful in estimating hydrate formation condition for mixture of sweet gas.

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

B. Temperature Depression

This is used to estimate the total amount of inhibitor methanol, ethylene glycol, diethylene glycol and triethylene glycol that is needed to be injected to inhibit hydrate formation. The total amount of inhibitor needed for hydrate inhibition is the amount that is in three phases namely aqueous liquid hydrocarbon, vapour and liquid hydrocarbon. Hammer-Schmidt equation is used to calculate the inhibitor concentration in the aqueous phases based on the assumptions that the effect of inhibitor 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 valid for natural gases with methanol concentrations 20-25wt% and 60-70wt% for glycol and the equation is expressed as:

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

C. Hydrate Formation Temperature

The hydrate formation temperature was determined from Katz plot curve fit equation at specific gas gravity. For this study, gas gravity of 0.56 was deduced and applicable. The Katz plot equation is expressed thus[8]:

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

D. Aspen-Hysys Simulator

The Peng-Robinson equation of state embedded in Hysys simulator is used for the three phase hydrate predictions. The simulator parameters such as pressure, natural gas composition, inhibitors and water content are defined and initiated in the simulator. The first or initial simulation is performed with no inhibitor and the resulting outcome is listed in Table 4 and plotted in figure 1 as reference temperature value for hydrate formation. Subsequently, other simulations were carried out for hydrate formation prevention by using inhibitors such as methanol, ethylene glycol, diethylene glycol and triethylene glycol, and the resulting outcomes and plots are shown in tables 5,6,7,8 and figures 2, 3, 4 and 5 respectively.

III. RESULTS ANALYSIS

The analysis of the result or outcome of Aspen-Hysys simulator applied in this study are highlighted as follows.

A. Hydrate Formation Temperature with No Inhibitor

The first simulation study was performed to deduce hydrate formation temperature of gas field A with no inhibitor and the result is shown thus.

TABLE IV: HYDRATE FORMATION TEMPERATURE WITH NO INHIBITOR

State	P(Bar)	T(°C)
1	0	-3.28E4
2	10	-3.28E4
3	20	2.41
4	30	5.97
5	40	8.42
6	50	10.51
7	60	12.21
8	70	13.61
9	80	14.78
10	90	15.79
11	100	16.66
12	110	17.44
13	120	18.13
14	130	18.76
15	140	19.33
16	150	19.85
17	160	20.33
18	170	20.78
19	180	21.20
20	190	21.60
21	200	21.97

Fig 1. Hydrate formation curve with no inhibitor.

B. Hydrate Formation Temperature with Methanol

Similar simulation was performed as stated above with the addition of methanol as an inhibitor to prevent the formation of hydrate and the resulting output is shown below.

TABLE V: HYDRATE FORMATION TEMPERATURE WITH METHANOL

State	P(Bar)	T(°C)
1	0	-3.28E4
2	10	-3.28E4
3	20	0.11
4	30	3.68
5	40	6.16
6	50	8.27
7	60	10.01
8	70	11.44
9	80	12.67
10	90	13.73
11	100	14.67
12	110	15.51
13	120	16.27
14	130	16.96
15	140	17.60
16	150	18.19
17	160	18.75
18	170	19.26
19	180	19.74
20	190	20.20
21	200	20.63

Fig 2. Hydrate formation curve with Methanol

C. Hydrate Formation Temperature with Ethylene Glycol

Also, Aspen-Hysys simulator was used to simulate the gas field parameters with ethylene glycol as an inhibitor to prevent or reduce hydrate formation temperature and the simulation result is shown below

TABLE VI: HYDRATE FORMATION TEMPERATURE WITH ETHYLENE-GLYCOL

State	P(Bar)	T(°C)
1	0	-3.28E4
2	10	-3.28E4
3	20	0.96
4	30	4.52
5	40	6.97
6	50	9.05
7	60	10.74
8	70	12.12
9	80	13.29
10	90	14.28
11	100	15.15
12	110	15.92
13	120	16.6
14	130	17.22
15	140	17.78
16	150	18.30
17	160	18.77
18	170	19.22
19	180	19.64
20	190	20.03
21	200	20.4

Fig 3: Hydrate formation curve with Ethylene glycol

D. Hydrate Formation Temperature with Diethylene Glycol

Diethylene glycol is added in this simulation operation as an inhibitor that mitigates hydrate formation and the resulting effect on hydrate formation temperature is shown thus

TABLE VII. HYDRATE FORMATION TEMPERATURE WITH DIETHYLENE GLYCOL.

State	P(Bar)	T(°C)
1	0	-3.28E4
2	10	-3.28E4
3	20	-0.32
4	30	3.23
5	40	5.67
6	50	7.74
7	60	9.42
8	70	10.79
9	80	11.95
10	90	12.94
11	100	13.79
12	110	14.55
13	120	15.23
14	130	15.84
15	140	16.39
16	150	16.90
17	160	17.38
18	170	17.81
19	180	18.23
20	190	18.61
21	200	18.98

Fig 4: Hydrate formation curve with Diethylene glycol.

E. Hydrate Formation Temperature with Triethylene Glycol

In this scenario, triethylene glycol is used as an inhibitor in the simulation of hydrate formation temperature and the resulting outcome is given below.

TABLE VIII: HYDRATE FORMATION TEMPERATURE WITH TRIETHYLENE GLYCOL.

State	P(Bar)	T(°C)
1	0	-3.28E4
2	10	2.89
3	20	8.07
4	30	11.39
5	40	11.97
6	50	13.51
7	60	15.47
8	70	16.09
9	80	16.55
10	90	17.21
11	100	17.76
12	110	18.24
13	120	18.66
14	130	19.03
15	140	19.38
16	150	19.69
17	160	19.99
18	170	20.27
19	180	20.54
20	190	20.80
21	200	21.05

Fig 5. Hydrate formation curve with triethylene glycol.

IV. DISCUSSION

Natural gas hydrate formation prevention through injection of chemical inhibitors have been a general practice in oil and gas industry as one of the techniques of mitigating hydrate formation, which is a hindrance or unwanted characteristic to flow and production in oil and gas industry. It can be deduced from this investigative study's simulation results that the introduction or injection of chemical inhibitors such as methanol, ethylene glycol, diethylene glycol and triethylene glycol leads to reduction of hydrate formation temperature at any specified operating pressure. This allows constant and adequate flow of gas within the system as flow assurance issues are mitigated against. It can be inferred from the study that the injection of any chemical inhibitor into the process, the hydrate formation temperature increases down the operational state as pressure increases with triethylene glycol yielding the highest hydrate formation temperature at 200bar.

Based on the determined study's data highlighted above and comparing hydrate formation temperatures with no inhibitor and chemical inhibitors, methanol as a chemical inhibitor gives the least hydrate formation temperature at any operating pressure in comparison with ethylene glycol, diethylene glycol and triethylene glycol respectively. In addition, methanol inhibitor shows the highest reduction deviation from the hydrate formation temperature process with no inhibitor with 95.5% deviation.

V. CONCLUSION

Hydrate formation is a serious flow assurance problem in oil and gas industry and its prevention or mitigation is of utmost importance to the industry for efficient flow and production operations. It can be deduced from this investigative study that hydrate formation prevention by chemical inhibitors is a mean of mitigating against flow assurance difficulties in oil and gas industry. Also, this study shows that application of chemical inhibitors methanol, ethylene glycol, diethylene glycol and triethylene glycol prevents hydrate formation by reducing hydrate formation temperature. In addition, it is also worthy to note that this investigative study did not account for the quantity or amount of different chemical inhibitors injected but with the application of Hammer Schmidt equation, the weight percentage range of chemical inhibitors is between 20-25 weight percent for methanol and 60-70 weight percent for glycols respectively.

NOMENCLATURE

MeOH: Methanol
 MEG: Monoethylene glycol
 DEG: Diethylene glycol
 TEG: Triethylene glycol
 SG: Specific gravity
 Yi: Mole fraction of component i
 Mw: Molecular weight
 ΔT : Temperature of depression
 M: Molecular weight of inhibitor
 C: Physical constants of inhibitor
 W: Weight percent of inhibitor
 MWair: Molecular weight of air
 P: Pressure
 T: Temperature
 CH₄: Methane
 C₂H₆: Ethane
 C₃H₈: Propane
 i-C₄H₁₀: Isobutane
 C₄H₁₀: Butane
 i-C₅H₁₂: Isopentane
 C₅H₁₂: Pentane
 C₆H₁₄+: Hexane plus

CO₂: Carbondioxide

N₂: Nitrogen gas

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