



Managing Hydrate Formation in Natural Gas Dominant Systems: A Systematic Approach

Wilfred Chinedu Okologume* and Chukwuebuka Okafor

Department of Petroleum Engineering, Federal University of Petroleum Resources, Effurun, Nigeria

*Corresponding Author: okologume.wilfred@fupre.edu.ng

ABSTRACT

This study evaluates the management of hydrate formation in natural gas dominant systems by incorporating equations which predict hydrate formation temperature of the natural gas at different pressure conditions. The study analyzed mathematical equation that predicts the hydrate formation temperature of the natural gas and subsequently estimates the inhibitor injection requirement that lowers the hydrate formation temperature. This was achieved using HYPI, a systematic tool/software developed for this purpose. From the result obtained, it was observed that as the pressure increases, the rate of increase of the hydrate formation temperature tend to decrease. Also as the temperature depression increases, it shows that the amount of inhibitor needed to depress the temperature to prevent hydrate formation also increases. HYPI was found to be accurate for determination of the hydrate formation temperature up to pressure of 4000 psia and temperature depression of up to 100 °F. Result from HYPI determination of hydrate formation temperature was compared and validated using results from Katz correlation. Overall, it was established that the HYPI software can be used for improved prediction of hydrate formation temperature and inhibitor estimate requirement for injected to prevent hydrate formation if need arises.

Key words: natural gas, hydrate, formation, inhibitor, temperature, pressure

INTRODUCTION

The Natural gas is considered to be a growing major energy source among the natural energy resources. Natural gas is widely available and is the cleanest-burning petroleum-based fuel [1]. Natural gas is a mixture of hydrocarbons such as methane (mainly), ethane, propane, butane and a few non-hydrocarbons such as hydrogen sulfide, carbon di oxide, nitrogen, etc. and water [2]; [3]. Natural gas hydrates (NGH) or Hydrates (as they are called) are ice-like crystalline compounds (molecular complexes) formed from mixtures of water molecule 'host' and suitably sized 'guest' gas molecules under pressure at considerable higher temperature than water freezing point [4]; [5].

The water (host) molecules, form lattice structures of several interstitial cavities with hydrogen bonding [6]. The guest gas molecule occupies the lattice cavities by forming hydrogen bond with the host water molecules [3]; [7]; [8]. When a minimum number of cavities are filled, the crystalline structure will become stable resulting in solid gas hydrates. Some conditions necessary for the formation of hydrate [4] include the right combination of pressure and temperature (low temperature and high pressure) [1], a hydrate former or guest molecule (e.g. methane, ethane, propane and carbon dioxide) and sufficient or the right amount of water (free water).

Statement of Theory

Natural gas dominant systems such as pipelines and process facilities are prone to hydrate formation and operators are continually on the lookout for possible hydrate formation conditions in the pipelines and facilities [10]. A characteristic problem with the production or transmission of natural gas, is the formation of gas hydrates [11]; [12]. This may eventually result to significant safety hazards to pipelines and process facilities and loss of man-hour (due to maintenance shutdown operations). Therefore, an understanding of the condition, prediction and inhibition of hydrates formation is essential to managing hydrate problems.

The specific gravity of the natural gas can be used to evaluate the hydrate formation temperature and pressure [13]. The Katz pressure-temperature curves for this purpose. The curve values are excellent for methane and specific gravity of gases less than 0.7 but it is not accurate for natural gas with specific gravity between 0.9 and 1.0 and it is also useless

for streams with sulphur compounds and larger molecules. The Equilibrium constant (k-value) hydrate formation estimation method which employs vapour-solid equilibrium constant (k-values) and pressure in the determination of the hydrate formation temperature [14]. It has vapour-solid values for methane, ethane, propane, iso-butane, neo-butane, carbon dioxide and hydrogen sulphide. This method gives appropriate and reasonable results for sweet natural gas up to 1000 psia.

A method used mostly to predict hydrate formation temperature of acid gases [5]. Range of application include total acid gas content 1-70%, H₂S content 1-50%, H₂S/CO₂ ratio 1:3-10:1, correction has to be made for C₃ content, chart is good for C₃ content up to 10%. It has advantage over the gas gravity and K-factor because it is design for use with sour gas. However, there have been some proposed correlation that are useful in the prediction and determination of the hydrate temperature and pressure [15]; [16]. A correlation for gas hydrate formation [17] as shown in the equation below:

$$T(^{\circ}\text{F}) = 8.9P\text{psi}^{0.285} \quad \text{eq. 1}$$

This easy to use equation does not take into account the effect of gas specific gravity.

Also, Makogon (1981) proposed a famous P-explicit correlation which was later modified by Elgibaly and Elkamel (1998) [18]; [19]. A modified form of the Makogon correlation is given below [20]:

$$\log P\text{Mpa} = \beta + 0.0497T(^{\circ}\text{C}) + T(^{\circ}\text{C})^2 - 1 \quad \text{eq. 2}$$

Consequently, this study developed a systematic approach for the management of hydrate in natural gas dominant systems/facilities using the highlighted existing thermodynamic analytical model equations.

METHODS

The computer model (HYPI) developed in this study is a simple petroleum engineering toolkit that aids in determining the hydrate formation temperature of natural gas at different operating pressure. It also helps to determine the amount of inhibitor (from a range of inhibitors) to inject in order to prevent hydrate formation. Some basic parameters which are used are given below in equations 3 to 5, as well as in Tables 1 to 4:

$$\log P_{(\text{Mpa})} = \beta + 0.0497(T_{(^{\circ}\text{C})} + kT_{(^{\circ}\text{C})}^2) - 1 \quad \text{eq. 3}$$

where,

$$A = 194.681789$$

$$B = 0.044232$$

$$C = 0.189829$$

$$P = \text{pressure in kpa}$$

$$T = \text{Temperature in kelvin}$$

$$x_m = 1 - \exp\left(\frac{-\Delta T}{72}\right) \quad \text{eq. 4}$$

where,

$$x_m = \text{mole fraction of the inhibitor}$$

$$\Delta T = \text{temperature depression in } ^{\circ}\text{C}$$

$$X_M = \frac{x_m M_m}{18.015 + x_m (M_m - 18.015)} \quad \text{eq. 5}$$

where,

$$X_M = \text{weight percent of the inhibitor}$$

$$M_m = \text{molar mass of the inhibitor}$$

Table-1 Natural Gas Components and Their Molar Mass

Components	Molar Mass (g/mol)
Methane	16.04
Ethane	30.07
Propane	44.10
i-butane	58.12
n-butane	58.12
Pentane	72.15
Carbon di oxide	44.01
Water	18.02
Nitrogen	14.01
Hydrogen sulfide	34.08

Table-2 Inhibitors used and their Molar Mass

Inhibitor	Molar Mass (g/mol)
Methanol	32.04
Ethanol	46.07
Ethylene glycol	62.07
Diethylene glycol	106.12
Triethylene glycol	150.17

In order to test the software, a stream of natural gas with the following composition and properties as presented in Table 3 was used.

Table-3 Compositions and Components of Natural Gas

Components	Percentage composition
Carbon di oxide	6.51
Nitrogen	5.97
Methane	76.62
Ethane	6.88
Propane	1.84
n-butane	0.25
i-butane	0.75
Pentane +	1.18

Minimum pressure = 100psia

Maximum pressure = 4000psia

Minimum temperature depression = 5°F

Maximum temperature depression = 100°F

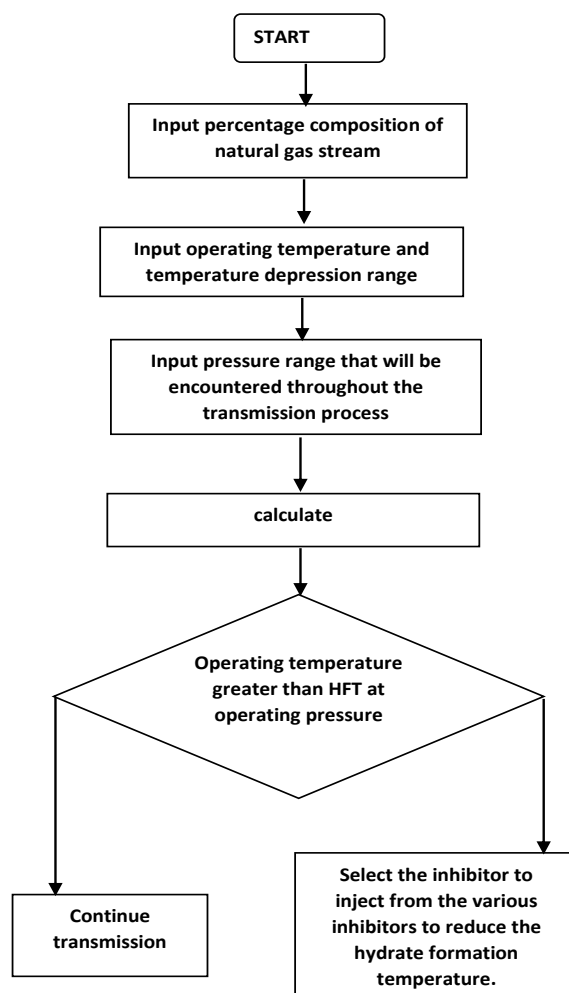


Fig. 1 The algorithm for HYPI

RESULTS AND DISCUSSION

Results

When the components of the natural gas stream are inputted in the software (as presented in the HYPI software start-up interface in Fig. 2), and using the presented analytical equations incorporated into the software, plots of pressure against hydrate formation temperature (presented in Fig. 3 to Fig. 9) were generated to show the hydrate formation curve obtained.

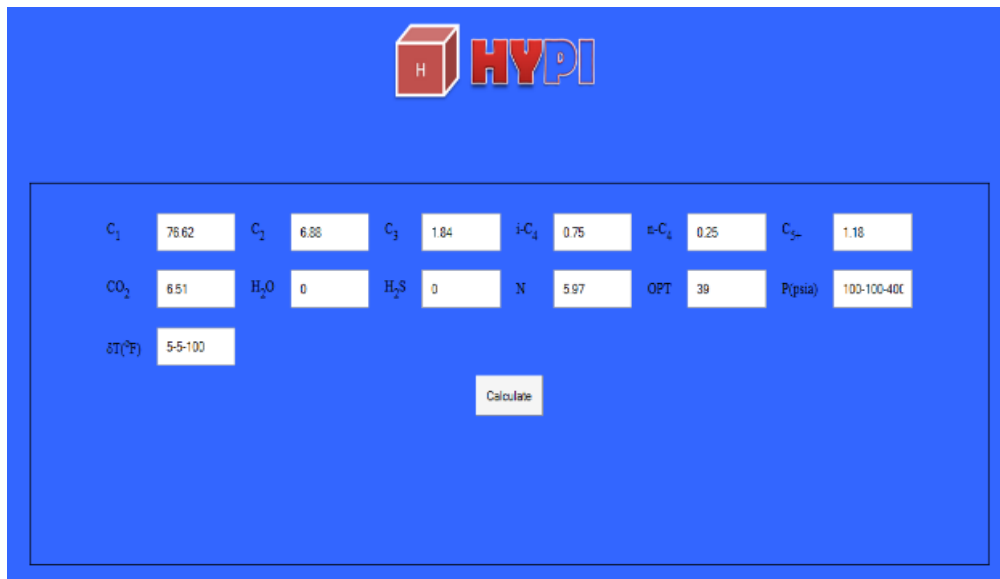


Fig. 2 HYPI Start-up page showing parameters

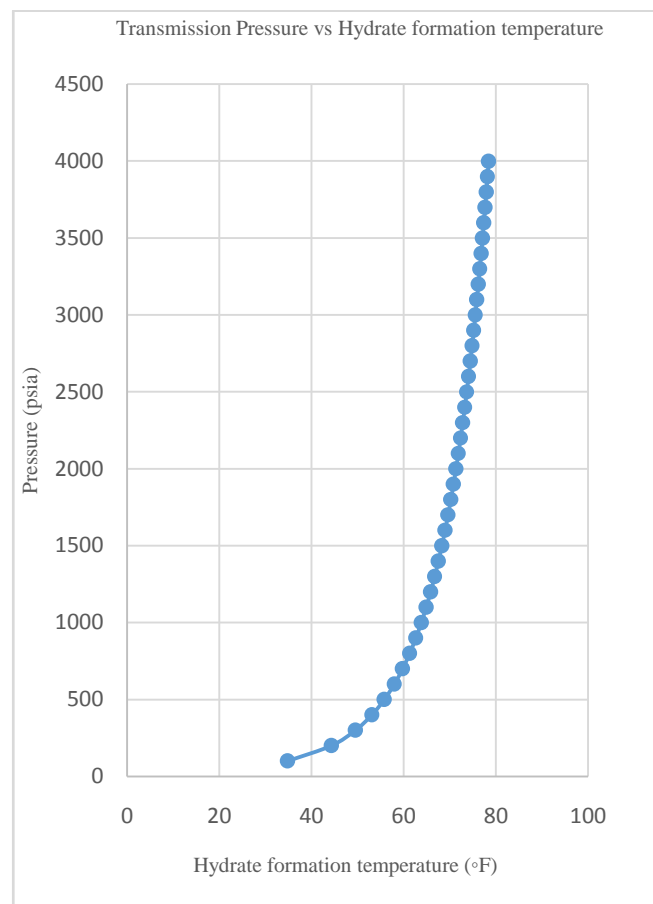


Fig. 3 Plot of pressure against hydrate formation temperature showing the hydrate curve to determine the hydrate and hydrate free region

Also from the inhibitor table (Table 2), a graph of temperature depression against percent weight of inhibitor is generated for all the considered inhibitors and presented in Fig. 4 to Fig. 8.

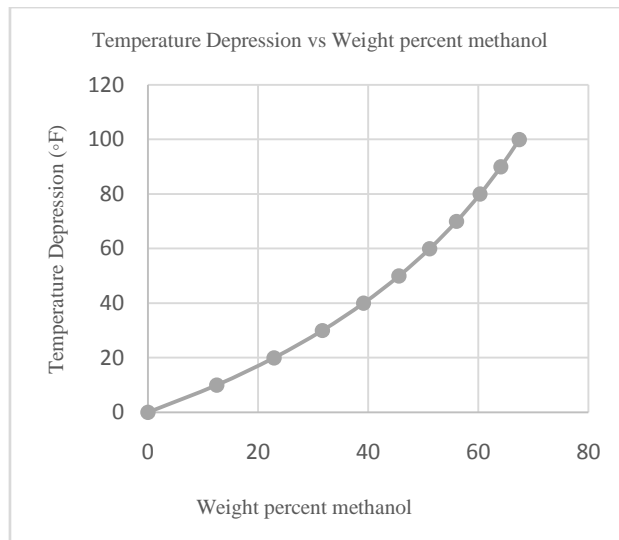


Fig. 4 Plot of temperature depression against weight percent of Methanol

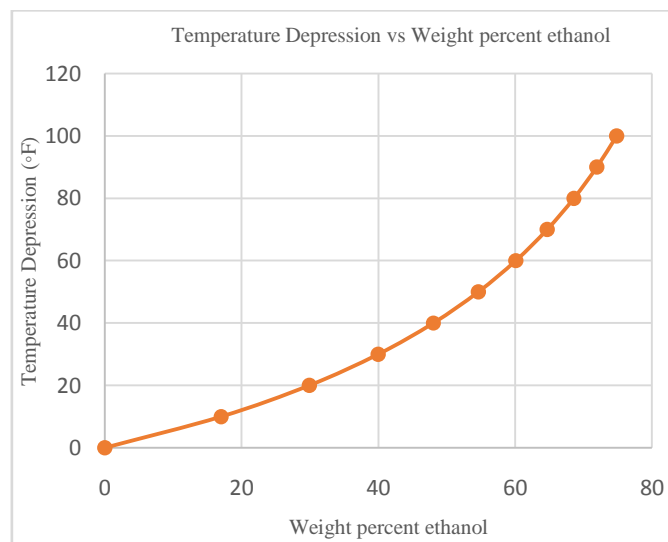


Fig. 5 Plot of temperature depression against weight percent of Ethanol

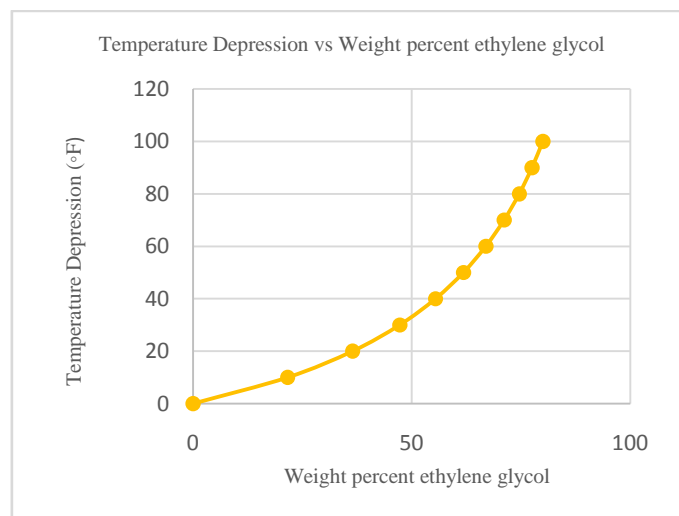


Fig. 6 Plot of temperature depression against weight percent of Ethylene glycol

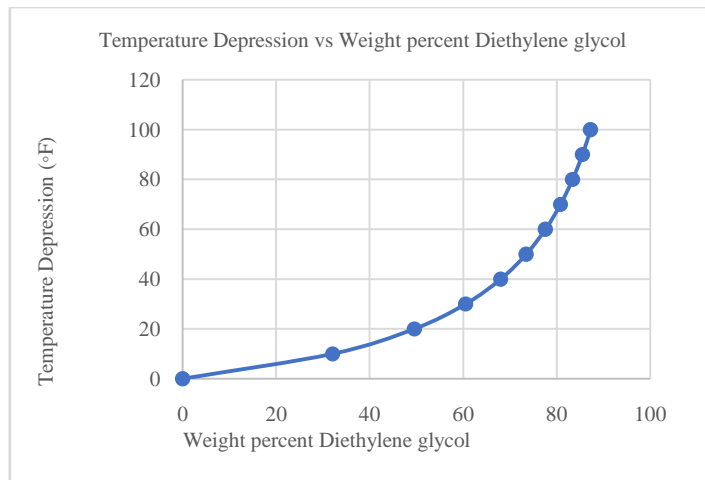


Fig. 7 Plot of temperature depression against weight percent of Diethylene glycol

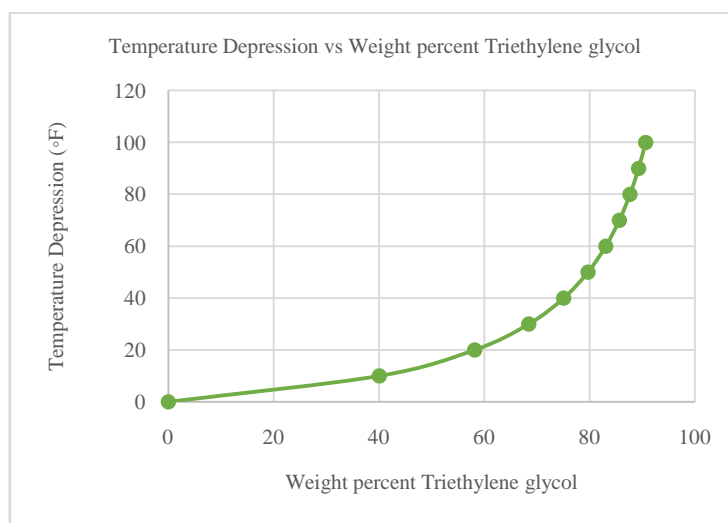


Fig. 8. Plot of temperature depression against weight percent of Triethylene glycol

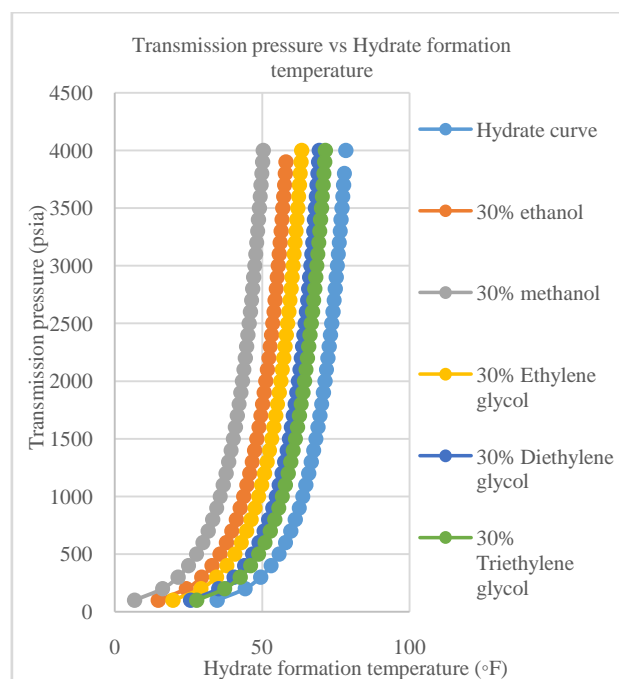


Fig. 9 Plot of transmission pressure against hydrate formation temperature showing the effect of 30% weight of the various inhibitors on the hydrate curve

Discussion

From Fig. 3, it can be seen that as the pressure increases, the rate of increase of the hydrate formation temperature tend to decrease. The region to the left of the curve in Fig. 3 is the hydrate formation region while the area to the right of the curve is the hydrate free region, natural gas transmission within that region will be hydrate free.

Also, From Fig. 4, 5, 6, 7, and 8, it shows that the amount of inhibitor needed to depress the temperature to prevent hydrate formation increase as the temperature depression increases. Different inhibitors have different inhibiting effect on the hydrate formation curve as shown in the results.

The results in Fig. 9 above illustrates the result when 30% of each inhibitor (methanol, ethanol, ethylene glycol, diethylene glycol and triethylene glycol) are injected and its effect on the hydrate curve and hydrate region. These inhibitors tend to shift the hydrate curve to the left decreasing the hydrate region and increasing the hydrate free region. This shows that as more inhibitor is injected, depending on the type on inhibitor, the hydrate curve tends to shift to the left thereby decreasing the hydrate region and increasing the hydrate free region. For instance, to achieve a temperature depression of 20°F about 23% of methanol, or 30% of ethanol or 37% of EG or 50% of DEG or 58% of TEG is needed. A key feature of this algorithm is that it predict the hydrate formation temperature at each transmission pressure throughout the transmission process and estimate the amount of inhibitor needed to suppress the hydrate formation temperature from a range of five thermodynamic inhibitors using a case study of the natural stream (Table 1 and Table 3).

CONCLUSION

This study successfully designed a computer program to predict the hydrate formation temperature of a natural gas stream; and estimating the amount of inhibitor to prevent hydrate formation. Based on the findings and observation of this study, the following deductions and conclusions are made:

- i. HYPI can be used to determine the hydrate formation temperature and estimate the amount of inhibitor to prevent hydrate formation if the need arises.
- ii. For determination of the hydrate formation temperature up to pressure of 4000psia, HYPI is accurate. HYPI is accurate for temperature depression up to 100°F.
- iii. When the same amounts of the different inhibitor are used to depress the hydrate curve, they show different inhibiting effect.

Different inhibitors have different effect on the hydrate curve. Methanol is more effective while TEG is least effective. Result from HYPI determination of hydrate formation temperature were compared and validated using results from Katz correlation. Also result from HYPI estimation of the amount of inhibitor to inject to depress the hydrate formation temperature were compared with that of Hammerschmidt and results were the same for methanol, ethanol, and ethylene glycol but different for diethylene and triethylene glycol. This difference was as a result of over estimation of the temperature depression of triethylene and diethylene by Hammerschmidt.

Recommendation

From the analysis of this study, the following recommendations are made:

- i. In order to ensure a good performance of the software, data should be accurately calculated and properly entered.
- ii. To prevent hydrate formation, natural gas should be transported at pressure and temperature which fall on the hydrate free zone.
- iii. The choice of the inhibitor to use will depend on several factors such as economics, availability effect on facilities and pipelines, ease of separation. e.t.c.
- iv. In order to achieve higher temperature depression with little quantity of inhibitor, methanol and ethanol are recommended.
- v. The amounts of inhibitor predicted by HYPI are only estimate. Proper analysis is required prior to injection.

REFERENCES

- [1]. W. C. Okologume, D.Appah, B. S. Kinigoma and E. J. Okafor, "Gas Hydrate Formation Promoted by Additives for Gas Storage Application: A Review" *Petroleum Technology Development Journal (PTDJ): An International Journal*, July 2019 - Vol. 9 No. 2. pp. 105 – 114.
- [2]. R. Kobayashi, Y. Song, E. D. Sloan and H. B. Bradley, *Petroleum Engineers Handbook*, Society of Petroleum Engineers, 1987.
- [3]. E. D. Sloan and C. A. Koh, *Clathrate Hydrates of Natural Gas*. 3rd edition. New York CRC Press, 2008.
- [4]. C. Baillie, and E. Wichert, Chart gives hydrate formation temperature for natural gas, *Oil & Gas Journal*,1987, 85(4), 37-39.
- [5]. W. I. Wilcox, D. B. Carson and D. L. Katz, Natural gas hydrates,*Industrial Engineering Chem*,1941 33, 662-671.
- [6]. P. Englezos, "Clathrate hydrates," *Industrial & Engineering Chemistry Research*, vol. 32, no. 7, 1993, pp. 1251–1274.

-
- [7]. E. D. Sloan, C. A. Koh, A. K. Sum, A. L. Ballard, G. J. Shoup, J. L. McMullen, J. Creek, and T. Palermo, Hydrates: State of the Art Inside and Outside Flowlines, *Journal of Petroleum Technology* distinguished lecturers' series, 2009, SPE 118534.
- [8]. M. Hossein, H. Ghafari, and S. Alavi, Molecular Dynamics Study of Guest–Host Hydrogen Bonding in Ethylene Oxide, Trimethylene Oxide, and Formaldehyde Structure I Clathrate Hydrates, *The Journal of Physical Chemistry*, 2017, 121 (16), 8832-8840.
- [9]. M. Motiee, "Estimate possibility of hydrate," *Hydrocarbon Processing*, Vol. 70, 1991.
- [10]. G. O. Ani1, C. E. Ubani A Systematic Approach in Determining Hydrate Formation in Natural Gas and Gas-to-Liquid Process Plants, *International Journal of Science and Engineering Investigations*, 2016, vol. 5, issue 58, 20–31.
- [11]. S. Mokhatab, R. J. Wilkens & K. J. Leontaritis, A Review of Strategies for Solving Gas-Hydrate Problems in Subsea Pipelines, *Journal Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 2007, 29: 1, 39-45.
- [12]. B. F. Towler and S. Mokhatab, Quickly estimate hydrate formation conditions in natural gases, *Hydrocarbon Processing*, Vol. 84, 2005.
- [13]. D. B. Carson, and D. L. Katz, *Natural gas hydrates*, Trans AIME, 146, 150-158, 1942.
- [14]. E. D. Sloan Jr., *Clathrate Hydrates of Natural Gases*, Marcel Dekker, New York, NY, USA, 3rd edition, 2006.
- [15]. Bahadori and A. Vuthaluru, A novel correlation for estimation of hydrate forming condition of natural gases, *Journal of Natural Gas Chem.*, 2009, Vol. 18.
- [16]. W. Okologume and D. Appah, "System Analysis for Predicting Gas Hydrate Formation", *International Journal of Advanced Research, IJAR*, 2018, vol. 6, issue 8, pp 735-743.
- [17]. E. G. Hammerschmidt, "Formation of gas hydrates in natural gas transmission lines," *Industrial & Engineering Chemistry*, vol. 26, no. 8, 1934 pp. 851–855.
- [18]. A. Elgibaly and A. M. Elkamel, A new correlation for predicting hydrate formation conditions for various gas mixtures and inhibitors, *Fluid Phase Equilibrium.*, 1998 Vol. 152.
- [19]. Y. F. Makogon, *Hydrates of Hydrocarbons*, PennWell, Tulsa, Oklahoma, 1997.
- [20]. B. Fu, S. Neff, A. Mathur, and K. Bakeev, Application of Low-Dosage Hydrate Inhibitors in Deep water Operations, *SPE Production and Facilities* (1), 2002, 133-137.