Hydrate formation calculation in the natural gas purification unit

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Abstract. Common problem in natural gas purification is Hydrate Formation. Hydrate is a solid – ice – like crystals in which gas molecules are trapped in the structure of solid water and causing problems especially clogging in the pipe line. Hydrate Formation usually happens at Dew Point Control Unit (DPCU) where the temperature is lowered to separate natural gas with heavy fraction by using Joule – Thomson effect. This paper aims to predict the Hydrate Formation Temperature at certain pressure by using some of HFT calculation methods. Kartz, Towler, Bahadori, and New Correlation are used to predict the Hydrate Formation Temperature with the pressure range of 700 – 2200 kPa. The obtained temperatures forming the gas at pressure of 700 kPa using Kartz, Towler, New Correlation, and Bahadori Calculation respectively are 274.26 K, 274.92 K, 275.02 K, and 275.2 K with Dew T at pressure of 700 kPa is 279.06 K, that means the Dew Point temperature is higher than the HFT, while at pressure 2200 kPa the temperature of Hydrate Formation respectively are 283.15 K, 283.46 K, 283.54 K, and 283.7 K with Dew T at pressure of 2200 kPa is 299.75 K, that means the Dew Point temperature is higher than the HFT.

1. Introduction

Nowadays, natural gas is widely used as main energy source besides oil and coal [1]. The sector that directly drives the increase in demand for natural gas is the electric power plant sector where natural gas has replaced coal and oil as the main fuel [2]. Natural gas produces fewer CO2, NOx, sulfur, dust and harmful substance emissions than coal and oil [3]. Before it can be stored and used as fuel, natural gas must undergo a process of purification. In this process one of the problems that often occurs is hydrate formation. Hydrate of gas is a solid – ice – like crystals in which gas molecules (mainly Methane) are trapped in the structure of solid water, which occurs when water molecules from a cage-like structure around smaller guest molecules [4]. The most common guest molecules are methane, ethane, propane, isobutane, normal butane, nitrogen, carbon dioxide, and hydrogen sulfide. Natural gas generally consist of propane, butane, and a little part of ethane and pentane [5]. It should be noted that normal butane does form a hydrate, but is very usable. While many factors influence hydrate formation are (1) the gas being at the appropriate temperature and pressure, and (2) the gas being at or below its water dew point, other factors that affect hydrate formation include mixing, kinetics, type of physical site, surface for crystal formation, agglomeration and the salinity of the system. Hydrate is first discovered by Davy in 1810. Villard in 1888 presented performance data on hydrocarbon hydrates. Although hydrates are known for over 200 years, their importance to the oil and gas industry was not realized until the 1930’s. In 1984, Hammerschmidt determined that hydrates were the cause of plugged natural gas pipelines, thereby leading to the regulation of gas water content, and the development of improved methods of prevention of hydrate plugs, including the injection of methanol and other inhibitors into the gas stream.
He developed the correlation that describes hydrate formation temperature as a function of only pressure. His simple correlation was modified by Ghiasi [6]. Formation behaviours of mixed gas hydrates including olefin compounds were addressed by Lee and Kang [7]. Some workers such as Jozian and Vafajoo [8] succeeded to build a mathematical modeling of the gas hydrate formation utilizing CFD technique.

2. Methods
In this research, Hydrate Formation Temperature was calculated using several methods, such as Gas Gravity Method [9], Towler & Mokhatab Calculation [10], Bahadori & Vuthaluru Method [11], and New Correlation which was done by Safamirazaei [12]. From several methods, some variables were changed such as (a) pressure on natural gas assumed to use ideal pressure on gas wells in Indonesia that is between 700-222 kPa, (b) Natural Gas molecular weight. In addition to predict the Hydrate Formation Temperature, Dew Point calculations were also made on natural gas based on the pressure influence between 700 - 2200 kPa pressure using Aspen Hysys Simulation Application and using 3 different fluid packages Peng - Robinson, Redlich - Kwong, and Lee - Kesler.

2.1 Gas Gravity Method
In 1945, Katz generated the gas gravity chart from a limited amount of experimental data and a more substantial amount of calculations based on the K-value method [9]. This plot relates the hydrate formation pressure and temperature with gas gravity defined as the apparent molecular weight of a gas mixture divided by that of air. To use this method, the gas should be primarily methane and other light hydrocarbons (ethane, propane, butane and normal pentane). Sloan showed in a statistical analysis report that this method is not accurate and the calculated pressure for the same gas gravity with different mixtures may result in 50% error. This method estimated the same hydrate formation pressure or temperature for the components having equal molecular weights, such as butane and isobutane, despite the fact that they should be different in reality. To avoid tedious calculations, a regression analysis was used to fit the curve to predict the hydrate developed for gases where specific gravity was known. Some available correlations for gas gravity method to calculate the hydrate formation conditions are Motiee correlation [13], Towler and Mokhatab correlation [10], and Bahadori and Vuthaluru correlations [11]. In which Bahadori & Vuthaluru correlation is the most accurate and reliable equation.

\[
\ln T = a + b \left( \frac{1}{P} \right) + c \left( \frac{1}{T} \right)^2 + d \left( \frac{1}{P} \right)^3 \quad (2)
\]

\[
\ln P = a + b \left( \frac{1}{T} \right) + c \left( \frac{1}{T} \right)^2 + d \left( \frac{1}{T} \right)^3 \quad (3)
\]

where,

\[
a = A_1 + B_1M + C_1M^2 + D_1M^3 \quad (4)
\]

\[
b = A_2 + B_2M + C_2M^2 + D_2M^3 \quad (5)
\]

\[
c = A_3 + B_3M + C_3M^2 + D_3M^3 \quad (6)
\]
\[ d = A_4 + B_4M + C_4M^2 + D_4M^3 \] (7)

This method helps to cover data from Katz gravity chart [13] in temperature variation of 260 K to 298 K as well as the pressures and gas molecular weights within the range of 1200 kPa to 40000 kPa and 16 g/mol to 29 g/mol, respectively. Although this correlation is accurate, its application is especially grueling and could be tedious. In this paper, a simple, easy to use and simultaneously accurate model for estimation of HTF is presented. Finally estimation capability of the obtained correlation and Bahadori & Vuthaluru [11] method is compared by some statistical parameters. The required data to develop this correlation includes the reported data for hydrate formation condition of natural gases as well as temperature and pressure. In this work, the hydrate formation condition is predicted rapidly by proposing a novel correlation, which has been developed, based on newly proposed numerical model. The following methodology has been applied to develop this correlation. Firstly, hydrate formation temperatures are correlated as a function of pressure for various molecular weights. Then, the calculated coefficients for these polynomials are correlated as a function of molecular weight. The derived polynomials are applied to calculate new coefficients for Equations (1) and (2) to predict the hydrate formation condition of natural gases as a function of pressure and temperature respectively. Table 1 shows the tuned coefficients for Equations (3) to (6).

2.4 New Correlation

Twenty-two experimental data points used by Bahadori and Vuthaluru [11], with specific gravities from 0.55 to 1, have been implemented to develop the correlation. Eq. 9 is suitable for estimating the HFT, especially for natural gas mixtures:

\[ T(K) = A\gamma^B(\ln P)^C \] (8)

This equation is the equation of the development of previous scientists, where by processing some data obtained by the determination of A B C as described above. Based on what M. Safamirzaei [12] does, according to him, New Correlation is the most effective method, because based on the % ARD value it calculates, New Correlation has the lowest %ARD with the least number of Adjustable Parameters compared to other calculation methods.

2.5 Dew Point Temperature

In some cases, the Hydrate Formation temperature is most commonly found in the Dew Point Control Unit where it separates natural gas from the heavy hydrocarbon component before entering the next treatment unit. The process used to reduce the temperature of natural gas to reach the dew point of the natural gas, that’s when the possibility of Hydrate formed, therefore it is necessary to review the relationship between Dew Point with temperature hydrate by calculating the dew point value of the natural gas. Dew point calculation method could be done in various ways, Dew Point is not influenced by the composition of the natural gas, dew point is only influenced by the pressure of natural gas.

3. Result and Discussion

Using different calculation methods, the results showed not too much different between each other, but the difference was quite significant when viewed from the difference between molecular weight with each other. The results of some calculations can be seen in Table 2. As we can see in the Figures 1 to 3, all of the results show a value that is not too much different, where the higher the pressure of natural gas Hydrate Formation Temperature will also increase, then between the pressure and temperature is directly proportional, it indicates that the four methods used to calculate the hydrate formation temperature is quite accurate, only need to be compared between the calculation data and actual conditions in the field.

From all of the calculation methods, the Bahadori Method always on the highest score overall, based on research conducted by Bahadori & Vuthaluru [11], they compared their results with actual data on the same operating conditions (Pressure and gas composition) which is not much different from each value (Calculated & Actual) with % Error between 0.01 - 0.2%.
Table 1. Tuned coefficients use in Equation (3) to (6) to Predict hydrate formation temperature in K (given pressure in kPa) by Equation (1)

| Coefficient | Natural Gas with molecular weight more than 23 & Pressure 1200 kPa < P < 40000 kPa | Natural Gas with molecular weight less than 23 & Pressure 1200 kPa < P < 5000 kPa |
|-------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|
| A1          | 6.418507                                                                         | -4.181213                                                                       |
| B1          | -8.801710 x 10^{-2}                                                             | 1.472639                                                                        |
| C1          | 3.557342 x 10^{-3}                                                              | -7.27458 x 10^{-2}                                                             |
| D1          | -4.749984 x 10^{-5}                                                             | 1.18979 x 10^{-3}                                                              |
| A2          | -8.642628 x 10^{3}                                                              | 4.528497 x 10^{4}                                                              |
| B2          | 1.024330 x 10^{3}                                                              | -6.862812 x 10^{3}                                                            |
| C2          | -4.096639 x 10^{4}                                                              | 3.424072 x 10^{2}                                                             |
| D2          | 5.445005 x 10^{-1}                                                              | -5.642533                                                                       |
| A3          | 1.159643 x 10^{7}                                                              | -8.317075 x 10^{7}                                                             |
| B3          | -1.385902 x 10^{6}                                                              | 1.260481 x 10^{7}                                                              |
| C3          | 5.535314 x 10^{4}                                                              | -6.301857 x 10^{5}                                                             |
| D3          | -7.339994 x 10^{3}                                                              | 1.040884 x 10^{4}                                                              |
| A4          | -4.020095 x 10^{9}                                                              | 5.858977 x 10^{9}                                                              |
| B4          | 4.791331 x 10^{8}                                                              | -9.663496 x 10^{8}                                                             |
| C4          | -1.903632 x 10^{7}                                                             | 5.134731 x 10^{7}                                                              |
| D4          | 2.511329 x 10^{4}                                                              | -8.878185 x 10^{5}                                                             |

It can indicate that the accuracy of Bahadori & Vuthaluru Method [11] is quite high. As for New Correlation method conducted by Safamirzaei [12] has advantages in the number of variables, it only needs 2 variables, and the variables are Pressure and Natural Gas molecular weight. It certainly simplifies the users of this method even though the accuracy of the method is still under Bahadori & Vuthaluru [11] method, with% error of 0.4%. As we can see in the Figures 1 to 3, all of the results show a value that is not too much different, where the higher the pressure of natural gas Hydrate Formation Temperature will also increase, then between the pressure and temperature is directly proportional, it indicates that the four methods used to calculate the hydrate formation temperature is quite accurate, only need to be compared between the calculation data and actual conditions in the field.

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Table 2. Predicted Hydrate Formation Temperature Results

| Pressure (kPa) | 22.8435 | 23.8473 | 20.4540 |
|---------------|---------|---------|---------|
|               | Kartz   | Towler  | New Cor. | Bahadori | Kartz   | Towler  | New Cor. | Bahadori |
| 700           | 274.6   | 274.9   | 275.0    | 275.2    | 275.3   | 275.6   | 275.8    | 275.7    | 273.5   | 273.5   | 273.7   | 273.4   |
| 850           | 276.2   | 276.5   | 276.5    | 276.9    | 276.8   | 277.1   | 277.3    | 277.2    | 275.3   | 275.3   | 275.9   | 275.6   |
| 1000          | 277.0   | 277.4   | 277.8    | 277.3    | 278.1   | 278.3   | 278.6    | 278.5    | 276.5   | 276.6   | 276.2   | 276.7   | 276.9   |
| 1150          | 278.4   | 278.5   | 278.8    | 278.3    | 279.2   | 279.4   | 279.6    | 279.7    | 277.6   | 277.7   | 277.3   | 277.8   | 277.9   |
| 1300          | 279.4   | 279.4   | 279.8    | 279.7    | 280.1   | 280.3   | 280.5    | 280.7    | 278.6   | 278.2   | 278.7   | 278.8   |
| 1450          | 280.1   | 280.2   | 280.6    | 280.9    | 280.9   | 281.2   | 281.4    | 281.4    | 279.4   | 279.1   | 279.5   | 279.8   |
| 1600          | 281.2   | 281.0   | 281.3    | 281.7    | 281.6   | 281.9   | 282.1    | 282.2    | 280.2   | 279.8   | 280.2   | 280.4   |
| 1750          | 281.8   | 281.7   | 281.9    | 281.9    | 282.4   | 282.6   | 282.7    | 283.0    | 280.9   | 280.5   | 280.9   | 281.5   |
| 1900          | 282.3   | 282.3   | 282.5    | 282.5    | 283.1   | 283.2   | 283.3    | 283.9    | 281.6   | 281.1   | 281.4   | 282.1   |
| 2200          | 283.0   | 283.5   | 283.5    | 283.7    | 284.1   | 284.3   | 284.3    | 284.8    | 282.6   | 282.3   | 282.5   | 283.0   |

Figure 1. Comparison of HET between each method, natural gas molecular weight: a) 20.454 b) 22.2875 c) 23.8437
As seen in Figure 2, the comparison of HFT values with molecular weight differences shows that the highest average HFT value occurs in Natural Gas with a molecular weight of 23.8473 and the lowest average HFT value occurs in natural gas with a molecular weight of 20.4541, indicating that the formation of hydrate gas is influenced by the molecular weight of natural gas, where HFT will increase as the molecular weight of natural gas increases or it can be said that both are directly proportional. The molecular weight of the natural gas is influenced by the composition of the natural gas, as the more composition of the heavy hydrocarbon in the natural gas, the molecular weight of natural gas will also be greater.

Table 3. Dew Point Results

| P   | Dew Point (K)     |
|-----|-------------------|
|     | Peng             | SRK   | Lee   |
| 700 | 280.2            | 281.2 | 280.9 |
| 850 | 283.5            | 284.9 | 284.7 |
| 1000| 287.0            | 288.0 | 287.9 |
| 1150| 289.7            | 290.9 | 290.7 |
| 1300| 292.0            | 293.0 | 293.2 |
| 1450| 294.1            | 295.1 | 295.4 |
| 1600| 295.9            | 296.9 | 297.4 |
| 1750| 297.6            | 298.6 | 299.2 |
| 1900| 299.0            | 300.1 | 300.8 |
| 2050| 300.4            | 301.5 | 302.3 |
| 2200| 301.6            | 302.7 | 303.7 |

As one can see in Table 3, results of Dew Point Calculation with several methods shows that when the pressure increases the dew point also increases. In Figure 3. shows that the results between one and other methods are quite similar, that means those calculation methods are valid. It is known, that the dew point is not affected by the composition of the components. It just depends on the pressure and the components. Figure 4 shows the comparison between Hydrate Formation Temperature and the average of dew point temperature.
As one can see the dew point values are above the Hydrate Formation Temperature, it means that the possibility of the hydrate to formed is low, it could happen because before natural gas reaches the Hydrate Formation Temperature, it will reach the Dew point temperature first which makes the natural gas will turn into the liquid phase.

This process sometimes happened in the Dew Point Control Unit in Natural Gas Purification. Hydrate Formation could be avoided as long as we keep the operation temperature between the Dew Point temperature and Hydrate Formation Temperature, in this case with Natural Gas Molecular Weight between 20-23, hydrate formation could be avoided by keeping the operation Temperature between 270°C – 280°C at Pressure 700 kPa – 2200 kPa. In other cases, the hydrate formation can be avoided by injecting chemicals such as DEG (Diethylene Glycol), MEG (Methyl Ethylene Glycol), and TEG (Triethylene Glycol).

4. Conclusion
Based on the results of the research that has been done, it can be concluded that the relation between Hydrate Formation Temperature and pressure of the natural gas is directly proportional. The higher the pressure of the natural gas, the higher the hydrate formation temperature is. The relation between Hydrate Formation Temperature and the natural gas molecular weight is directly proportional. The higher the natural gas molecular weight, the higher the hydrate formation temperature is. The relation between Hydrate Temperature Formation and Dew Point temperature is if the dew point temperature is above the hydrate formation temperature, then the possibility of the hydrate formed is low.
Acknowledgement

The authors announce that this research was funded DIKTI through PMDSU Project No. 042554/IT2.11/PN.02/2016.

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