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Comparative analysis of Hammerschdmit correlation, Towler and Mokhatab Correlation, Katz chart, and Hysys simulation in predicting Hydrate formation Temperature for a methane-ethane binary system.

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ABSTRACT: *Gas hydrates are very stable ice-like structures that form at elevated pressure and low temperature in the presence of water and gas. Gas hydrate formation has plagued the petroleum industry for years due to its ability to plug the flow line and stop flow of fluid. Mitigating hydrate blockage in pipes costs the petroleum industry millions of dollars annually. It is important to adequately predict the hydrate formation thermodynamic conditions so that proper mitigation plans can be made before hydrate formation/deposition commences in the flow system. This study compares four different hydrate prediction methods; Computer simulation using Hysys, Hammerschdmit correlation, Towler and Mokhatab correlation and Katz chart. These methods were used to predict hydrate formation conditions for methane-ethane binary gas systems with varying mole fractions of methane (56.4%, 90.4%, 95.6%, 97.1%, and 98.8%).It was discovered that the computer correlation had the least prediction error in all the methane-ethane binary systems considered in this work. Therefore, it performed best. The Katz plot prediction improved (decreased prediction error) with increasing concentration of methane while the Towler and Mokhatab correlation as well as the Hammerschdmit correlation prediction error increased with increasing methane content. In the absence of a Hysys simulator, the engineer must choose a good correlation for adequate hydrate prediction in a methane-ethane binary system based on the gas composition.*

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I. INTRODUCTION

Hydrates are ice-like crystalline structures which are found in the reservoir as well as in production and gathering systems. Hydrates consists of a mixture of gas molecules and water molecules. The gas molecules (also called guest molecules) are trapped in cavities formed by the water molecules.

Hydrates exist in different crystallographic types (or structures) and these are: structure I, structure II and structure H. Structure I hydrates are those that allow only the inclusion of methane, ethane and carbondioxideas guest molecules within the cavities formed by the water molecules and contain about 46 molecules of water; while structure II hydrates are those that permit the inclusion of compounds like propane, isobutane, nitrogen, and contain about 136 molecules of water. The third hydrate structure which, unlike the other types, has an indefinite structure allows the inclusion of higher molecular weight hydrocarbons like iso-pentane, as well as other gases like H_2S, CO_2, CH_4, Xe, etc. Irrespective of the structure, gas hydrates may cause irreparable damages, hazardous conditions and even production shut down when not properly managed.

Whenever water and guest moleculesexist at specific conditions of temperature and pressure, usually high pressures and low temperature, hydrates are likely to form. In the oil industry, hydrates are a major encumbrance to smooth running of production and transmission facilities, as they can block flow lines and process equipment(Sloan, 1998).

Iyowu (2010)suggested that hydrate control can be approached in two ways: the preventive approach and the corrective approach. Hydrate preventive approach involves preventing the actual formation of gas hydrates maintaining the system pressure below the hydrate formation pressure, maintaining the system temperature above the hydrate formation temperature using thermal insulation or heating,dehydrating to remove

water from the system and the use of chemicals that prevent hydrate formation.The corrective approach is done to remove already formed hydrates. This can be done by the use of mechanical pigs, heating to melt hydrates and the use of chemicals that melt hydrates. The preventive approach is usually is preferable to the corrective approach of hydrate management as it prevents downtime and helps maximize profit. It is also safer because hydrate can act as a projectile and rupture the pipe during hydrate dissociation.

Accurate estimation of hydrate formation conditions is essential for effective hydrate prevention. The prediction of the thermodynamic conditions necessary for the formation of Natural Gas Hydrates(NGH) can be done in three ways:Experimental study, Empirical methods and the use of Computer software simulation.

The experimental study of NGH is divided into the macroscopic, mesoscopic and microscopic experiments (Sloan and Koh, 2007). Experiments should be conducted at high pressure and low temperature to model the actual field conditions and these conditions of temperature and pressure may pose some safety hazard to laboratory personnel. Hence, the Empirical method and Computer Simulation method are safer and cheaper ways of predicting hydrate formation as they can predict hydrate formation at high pressure and low temperature safely without the use of experimental apparatus.

HYSYS is one of the oil industry's leading process simulator. The hydrate prediction utility in HYSYS works by collating the inputs conditions of the stream and fluid composition to compute the hydrate formation temperature and the hydrate type formed (Type I or Type II).

The hydrate formation experimental data (temperature and pressure) points for this research were obtained from Deaton and Frost (1946) experimental data for a binary gas system of methane and ethane. The experimental data contains 22 data points consisting of different percentages of methane. The temperatures and pressures were converted to degrees Fahrenheits (^oF) and psia respectively.This work compares hydrate prediction using a simulator, Hysys and three different empirical methods coded in excel spread sheet.

1) Hammerschmidt (1934), proposed a correlation for the prediction of hydrates as given in equation 1.

$$T(°F) = 8.9P^{0.285}(psi) \quad (1)$$

2) Towler and Mokhatab (2005) proposed a correlation for predicting hydrate formation temperature in terms of specific gravity and operating pressure (Equation 2).

$$T_{(^oF)} = 13.47\ln P_{(psi)} + 34.27\ln Y - 1.675\ln Y \ln P_{(psi)} - 20.35 \quad (2)$$

3) The Katz chart prediction method assumes that sufficient water is present to form a hydrate. Thus, the mole fractions in this method are on a water-free basis.Owodunni&Ajeinka (2007) digitized the Katz chart and gave the curve fit equation 4, equation 5 and equation 6

For gas specific gravity of 0.554:

$$T = 15.781 * \ln(P) - 60.679 \quad (4)$$

For gas specific gravity of 0.6:

$$T = 13.055 * \ln(P) - 31.29 \quad (5)$$

For gas specific gravity of 0.7:

$$T = 12.116 * \ln(P) - 20.818 \quad (6)$$

II. METHODOLOGY

To run the Hysys simulation, the components of the gas in this study (Methane and Ethane) were selected to make up the gas composition. The Peng-Robison equation of state which is best suited for hydrocarbon systems was selected. A material stream having the gas components was selected and the pressure and temperature values of the stream were imputed in the simulation environment. They hydrate utility tool was then used to predict the hydrate formation temperature for the inputted operating pressure.

A spread sheet was developed to calculate the hydrate formation temperatures at different pressure using the Hammerschmidt, Towler and Mokhatab, and Katz correlations.The spreadsheet was also equipped to estimate the error between experimental and predicted values obtained from Hysys simulation and the various correlations used in this study.

Data inputedto the spread sheet include gas composition, and the experimental hydrate formation temperatures for the different pressures considered. The spreadsheet calculates the specific gravity of the gas based on the composition given and further estimates the hydrate formation conditions using theHammerschmidt, the Towler and Makhatab and the Katz chart correlations.

III. RESULTS

A plot of pressure against time for the methane-ethane binary system with 56.4wt% of methane (Figure 1) shows that the Hysys prediction closely approximates the experimental data. The Hammerschmidt correlation

over predicted hydrate formation conditions in this system and the Katz plot underpredicted the hydrate formation temperatures (Figure 1).

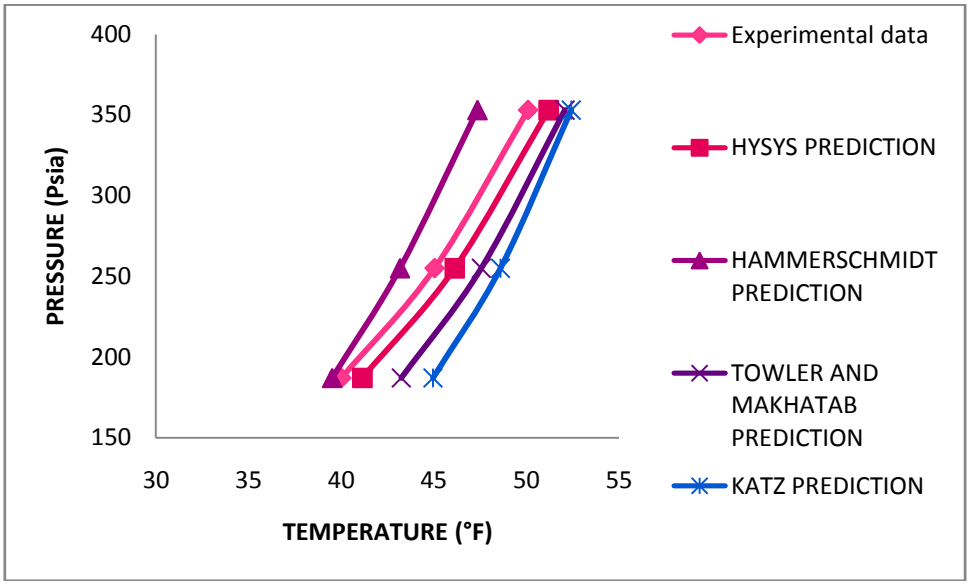

Figure. 1: Hydrate equilibrium curves for 56.4% CH_4

As the methane composition increased to 90.4wt% in the ethane-methane system, Hysysslightly over predicted the hydrate formation conditions (Figure 2) while all the empirical correlations used in this study under predicted hydrate formation conditions. The closest of the empirical correlation to the experimental data is the Katz plot (Figure 2).

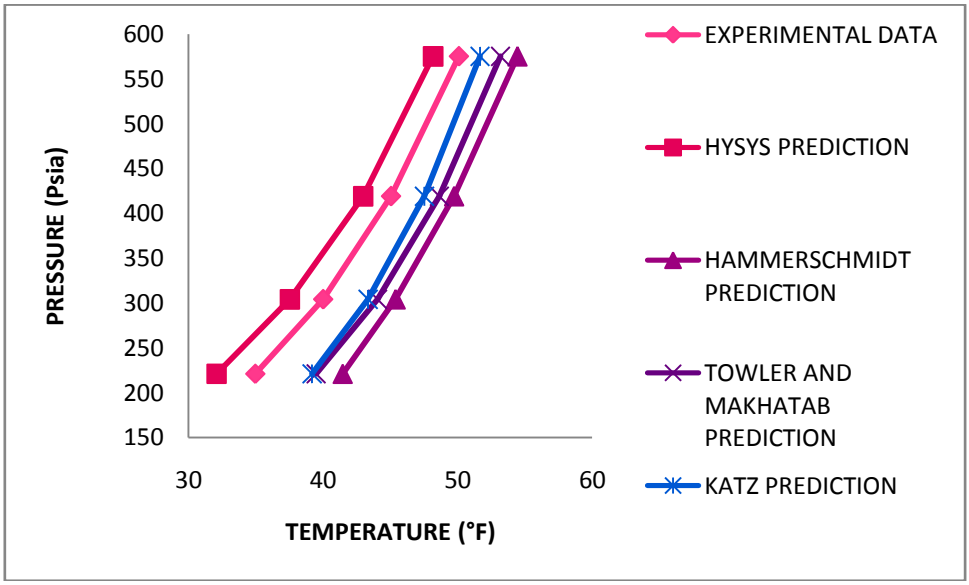

Figure 2: Hydrate equilibrium curves for 90.4% CH_4

Further increase in methane content to 95wt% showed same trend of Hysys over predicting experimental data and the empirical correlations under predicting hydrate formation conditions (Figure 3). Katz Chart and Towler and Mokhatab correlation hydrate formation predictions were closely matched at pressures between 200 psia and 300psia (Figure 3).

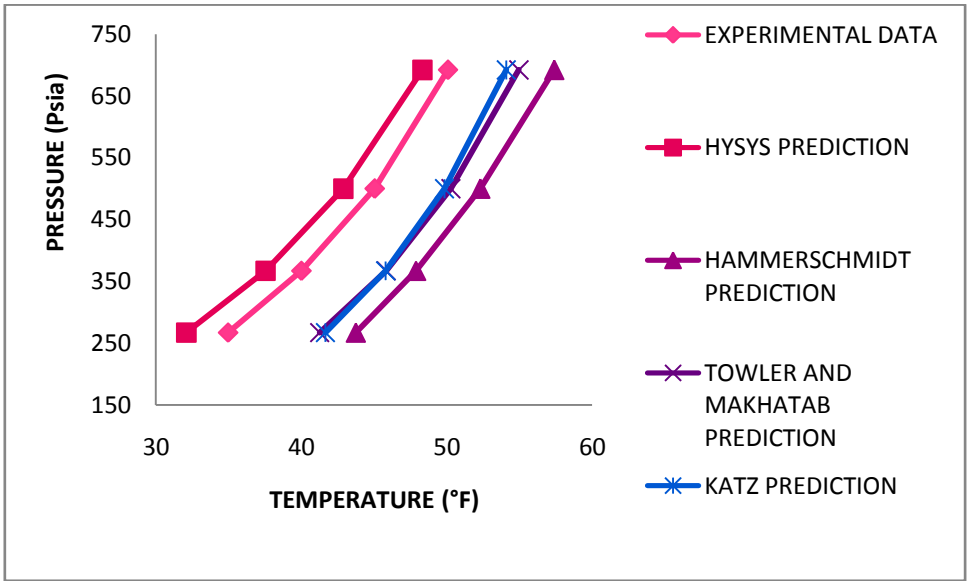

Figure. 3: Hydrate equilibrium curves for 95% CH_4

Further increase in methane content to 97.1% and subsequent reduction in ethane content in the methane-ethane binary gas system showed Katz plot over predicting hydrate formation conditions (Figure 4), Hysys simulation also slightly overpredicted hydrate formation temperatures at this gas composition. However, Towler and Makhatab correlation and Hammerschmidtcorrelation largely under predicted hydrate formation conditions in this system.

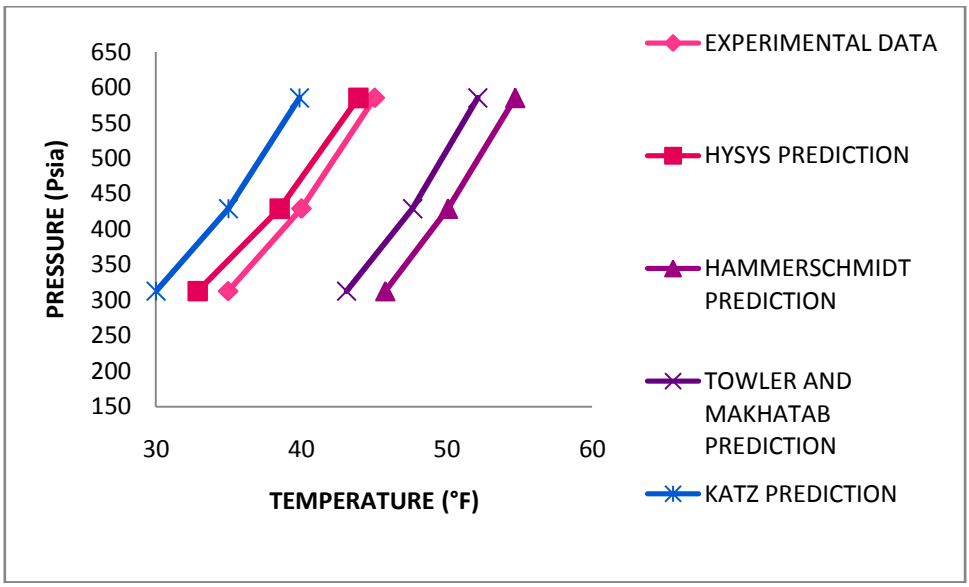

Figure 4: Hydrate equilibrium curves for 97.1% CH_4

With further increase of methane content to 97.8wt% of methane in the methane-ethane binary gas system, hydrate formation condition was over predicted once again by katz plot while the Hysys simulation was a very close match to the experimental data (Figure 5).

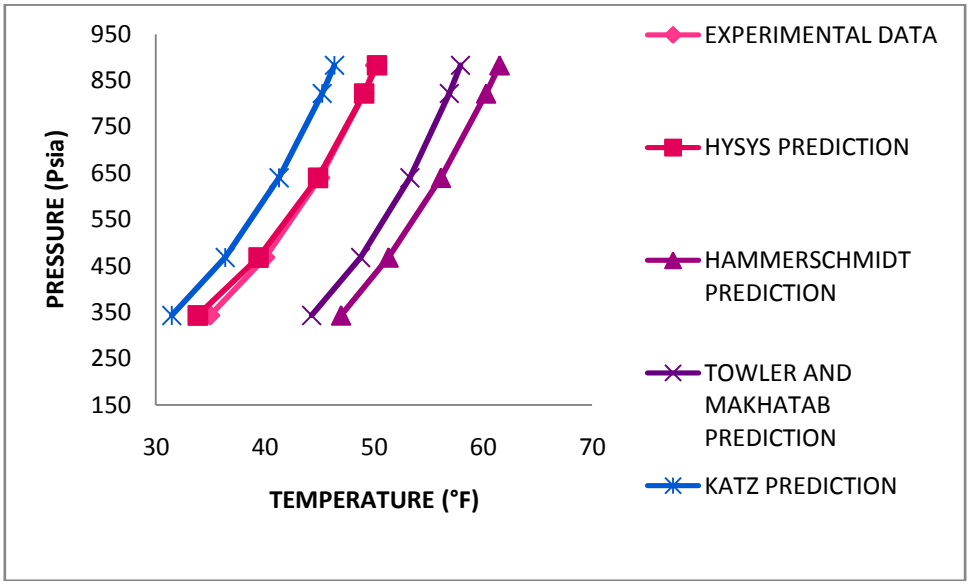

Figure 5: Hydrate equilibrium curves for 97.8% CH_4

At the maximum methane content (98.8wt% methane) considered in the experiment by Deaton and Frost (1946), Katz plot slightly over predicted the hydrate formation conditions (Figure 6) however, Hysys and the two other correlations under predicted the hydrate formation conditions.

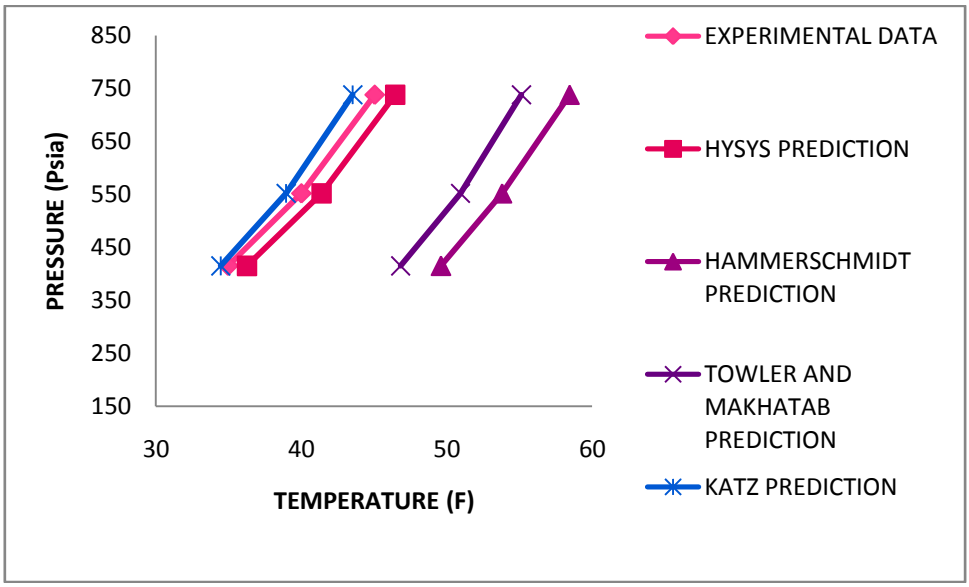

Figure6: Hydrate equilibrium curves for 98.8% CH_4

Notice that as the methane-ethane binary system tended towards a single pure gas (methane), Katz plot became a better prediction tool. This is because one of the curves in Katz chart was obtained from experimental data of pure methane gas. An analysis of the prediction error will give a further insight on the performance of each method.

Error Analysis

The errors in the different prediction methods were computed by calculating the absolutedifference between the predicted temperatures and the experimental hydrate formation temperatures for the various compositions of the methane-ethane binary system usingequation 7.

$$T_{aad} = \sum_{i}^{n} \left| T(\text{cal.})_i - T(\text{exp.})_i \right| / n \qquad (7)$$

Where n is the number of data points.

Error analysis results for the different gas compositions considered in this work are outlined in Figures 10 to Figure 15.When the methane composition was 56.4wt%, Hysys was the best performing prediction method while Katz plot was the least performing prediction method (Figure 7). With an increase in methane composition to 90.4wt%, Hysys still had the least prediction error and Hammerschdmit correlation had the most prediction error (Figure 8).

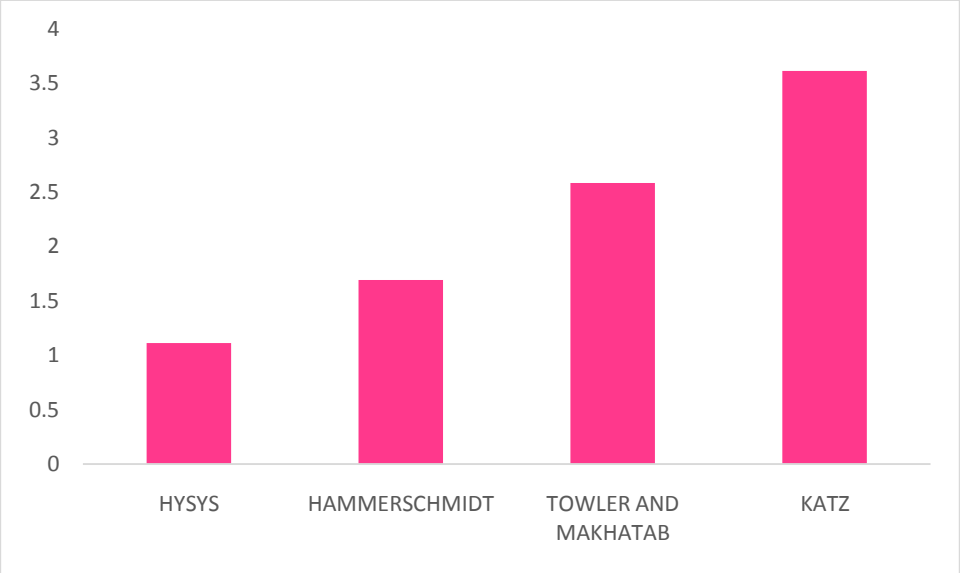

Figure7: Mean of absolute temperature difference for56.4% CH_4

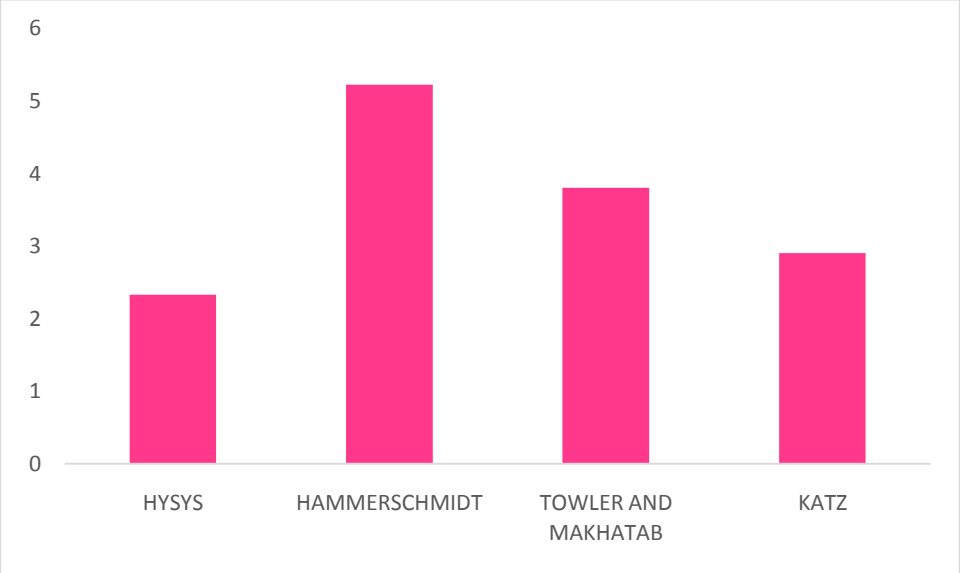

Figure 8: Mean of absolute temperature difference for90.4% CH_4

Further increase in methane composition to 95.6% still gave Hysys as the best performing prediction method with less error and Hammerschmidt correlation as the worst performing prediction method due to its large error (Figure 9). Increasing the methane compositiononce again to 97.1% methane showsHysys as the best prediction method however, and Katz plot is the second best prediction method although it still had a relatively large prediction error (Figure10). The worst performing prediction method in this composition was Hammerschdmit correlation.

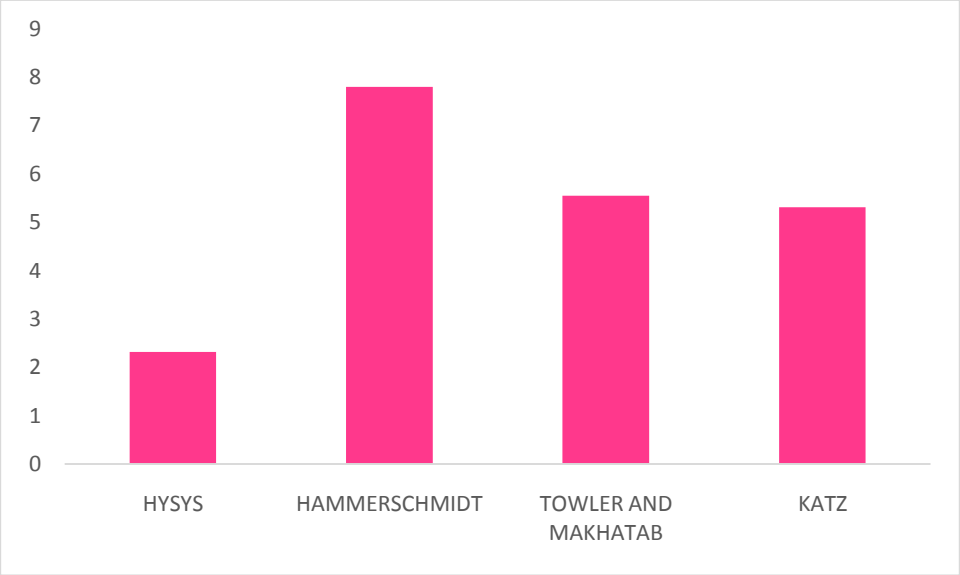

Figure9: Mean of absolute temperature difference for 95.6% CH_4

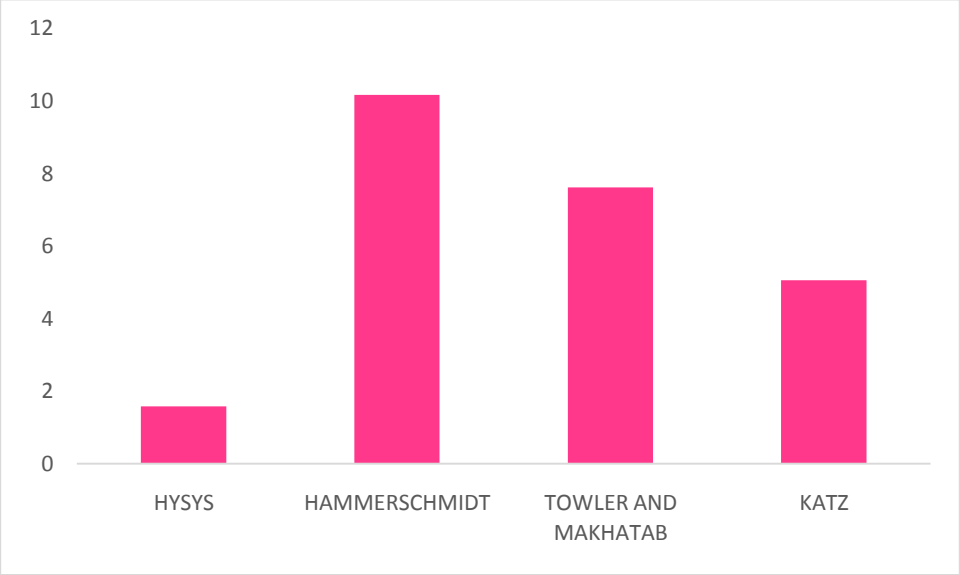

Figure 10: Mean of absolute temperature difference for97.1% CH_4

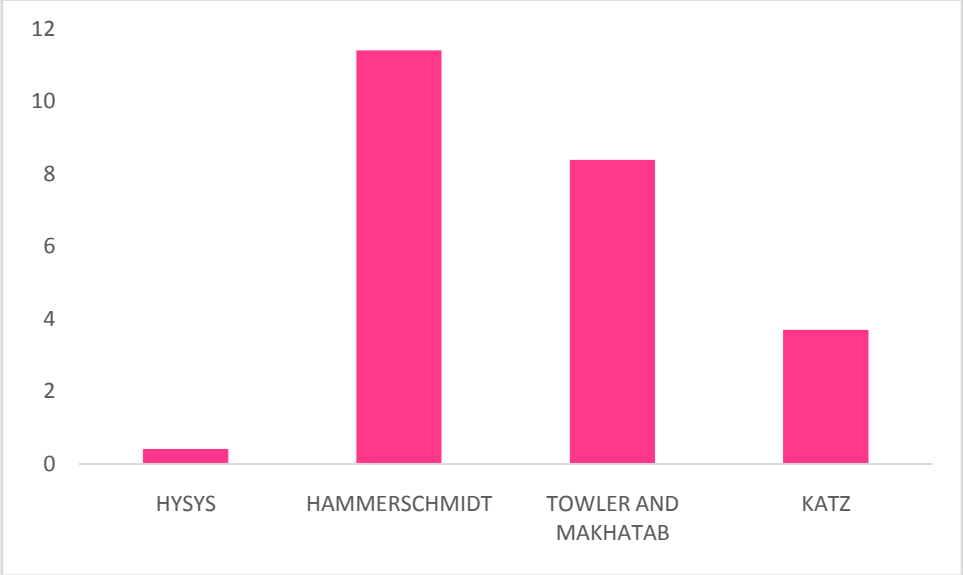

Figure 11: Mean of absolute temperature difference for97.8% CH_4

In the ethane-methane binary system with methane composition of 97.8wt%, Hysys had very little prediction error and the next best performing method was Katz plot (Figure 11).At methane concentration of 98.8%, Hysys had a minimal prediction error followed by the Katz plot (Figure 12).

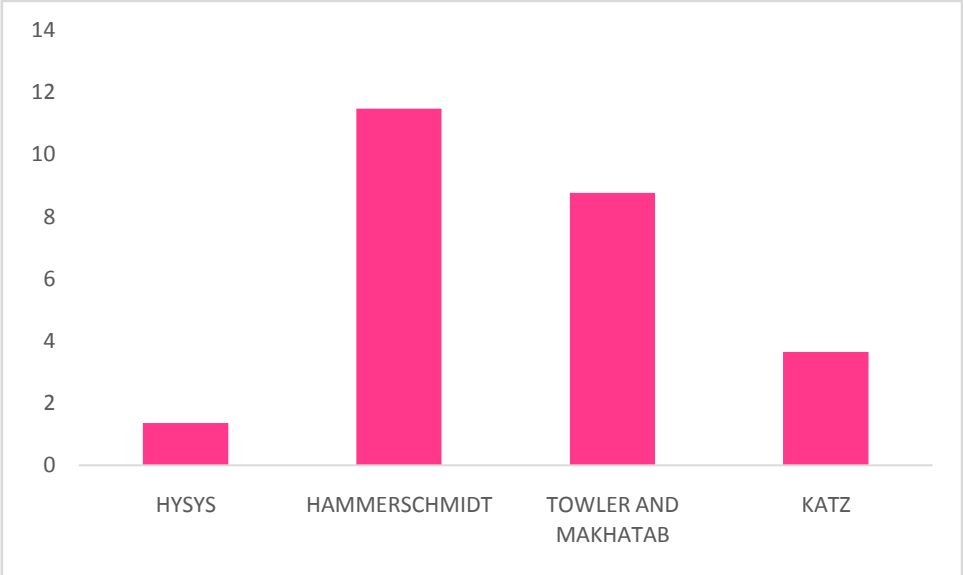

Figure 12: Mean of absolute temperature difference for98.8% CH_4

Note that the error obtained from the Hammerschmidt correlation and the Towler and Makhatab correlation increased with increasing concentration of methane. When methane composition was 56.4%, the prediction error for Hammerschmidt correlation was 1.7 while that of Towler and Makhatab was 2.6 (Figure 7). As methane concentration increased to 90.4%, the prediction error for Hammerschmidt correlation increase to 5.6 while that of Towler and Makhatab was 3.6 (Figure 8). Figure 9, Figure 10 and Figure 11 showed similar trend of increasing prediction error with increasing methane composition. In the highest methane composition considered which is 98.8%, the predictionerror of Hammerschdmit had increased to 11.3 while that of Towler and Makhatab had risen to 8.7 (Figure 12).

IV. CONCLUSION

The essence of predicting hydrates formation conditions is to ascertain when hydrates will likely form and propose proper hydrate management plans in order to alleviate flow assurance problems. This study has shown that Hysys simulation method was a better prediction tool compared with the other correlations considered in this work. However, where the software isnot available, Katz plot prediction is more accurate for methane-ethane binary system with low ethane composition and the effectiveness of Towler&Mokhtab and Hammerschdmitcorrelation in predicting hydrate formation temperature reduces with increase in methane content in a binary methane-ethane system

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