Evaluating the Relationship Between Natural Gas Hydrocarbon Heavy-Ends Condensation and Its Hydrocarbon Dew Point HDP

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Abstract

Natural gas comprises of non-hydrocarbons, light and heavy-end hydrocarbons. Although heavy-end hydrocarbons, may be present in negligible concentration in dry or lean gas, its reasonable occurrence in wet or rich gas is of great concern to all stakeholders because of their ability to retrograde and coalesce into liquid or solids.

Hydrocarbon Dew Point is basically controlled by the availability and quantityof condensable heavy-end hydrocarbons in a natural gas sample. In this work, fifteen natural gas samples, collected from different flow stations and gas processing plants in the Niger Delta Region were used. In this exercise, efforts were made to establish the relationship between the liquid content of the gas or condensable hydrocarbon and the resultant measurable hydrocarbon dew point of the same natural gas sample.

The natural gas samples were analyzed by Gas Chromatographic technique in reference to ASTM D1945 (2013). The results generated were reported in gallons per thousand cubic feet (GPM) of various alkane plus fractions. HDP was measured with manual dew-scope, using ASTM D1142 as standard method. NIST 1297 and Statistical tools were used to quality-check generated analytical results.

The results of this work confirmed that there is a relationship between condensable hydrocarbons and practical hydrocarbon dew point. It also highlighted the need to employ gas chromatographic method as a tool to give a vivid picture of the condensable heavies that resulted in the measured HDP.

Introduction

HDP is the temperature (at a given pressure) at which the hydrocarbon components of any hydrocarbon-rich gas mixture, such as natural gas will start to condense out of the gaseous phase. In natural gas it is an important qualitative parameter, usually stipulated in contractual specifications and enforced throughout the supply chain, from producers through transmission and distribution companies to final end users (Andy Benton, 2007). HDP is the temperature at which hydrocarbon condensates first begin to form when natural gas is cooled, at constant pressure and thus ceases to be wholly gaseous.

The extent to which a given natural gas sample condenses is greatly influenced by reticulation of its heavy-ends hydrocarbons. Condensable components of hydrocarbons are usually estimated as Natural Gas Liquids (NGLs), Liquefied Petroleum Gas (LPG), Gallon per Million/SCF (Standard Cubic Feet) of

various plus fractions. The possible negative impact of condensable hydrocarbons in natural gas mixture, which include but not limited to increased pressure drop, hydrate formation, equipment damage and reduced line capacity.

HDP can be either be measured manually by manual-visual technique with chilled mirror dew scope or by automatically by optical condensation dew scope. Also, it can be calculated from extended composition by gas chromatography.

Despite the capabilities of the aforementioned techniques to measure HDP temperatures of natural gas mixtures, they cannot vividly detail the proportion of heavies that produce the condensation.

In this exercise, efforts were made to establish the relationship between the liquid content of the gas or condensable hydrocarbon and the resultant measurable hydrocarbon dew point of the same natural gas sample. Fifteen natural gas samples, collected from different flow stations and gas processing plants in the Niger Delta Region, were used for this study.

The condensable hydrocarbon component results generated were reported in gallons per thousand cubic feet (GPM) of various alkane plus fractions were compared with their respective measured dew point, This result served as pointer to know when the measured hydrocarbon dew point results were not appropriately determined or out of trend and logical premise to evaluate quality check efficiency of the instrument.

Methods

This encompassed sampling, sample preparation, analysis and quantification. A good QA/QC was observed throughout the entire process.

Sampling

The objective of any sampling procedure is to obtain a representative sample from the system under investigation (GPA 2166-05).

Two sampling approaches were employed in this work, that is in-situ and spot natural gas sampling. Both sampling procedures complies with API MPMS CH 14.1-06 and GPA- 2166-05

Good sampling operation program should involve selecting corresponding source, obtaining enough sample volume for analysis, maintaining sample integrity and transportation of sample to laboratory for analysis. (Mmata et al. 2011)

Prior to field sampling campaign, gas cylinders were usually washed with cleaning solvent, pressure tested, dried with compressed air and properly vacuumed. At the point of gas sampling, the prepared bottle was connected to the sampling source, and flushed severally with the intended sample for collection. About 500cc of the sample was collected into the sample cylinder, properly capped and correctly labeled as per sample source. Duplicate samples were collected from each sampling point as part of quality assurance.

Sample Preparation

On arrival to the laboratory the details of the samples were logged into the sample reception register. Opening pressure check was carried out to confirm sample integrity at laboratory conditions. Samples that were intact were restored to sampling conditions and analyzed.

Analysis

This comprised of laboratory analysis and On-site measurement.

Laboratory Analysis

The restored gas sample was analyzed with Agilent 7890B; state-of-the-art gas analyzer, equipped with Thermal Conductivity Detector (TCD) and a Flame Ionization Detector (FID). It also has Packed and Capillary columns. Molecular sieve and Haysep-Q were the packed columns while PONA was the

capillary column used. The oven program was at initial temperature of 60° Cheld for 28.7 mins and then increased to 100°C ata rate of 13°C/mins and kept at temperature for additional 4 minswith a total run time of 38mins. Helium was used as the carrier gas.

CO_2, O_2 and N_2 which areall non-hydrocarbons were separated in the packed column while hydrocarbons like CH_4 to $C_{10}H_{22}$ were separated in the capillary column. The separated components were detected by the detectors namely the FID for hydrocarbons and TCD for non-hydrocarbons. Prior to the analysis the GC was calibration with standard gas to enable identification of the gas components in the natural gas samples and to determine the response factors of each component. This procedure complies with ASTM D 1945-14. The peak area was proportional to the concentration or amount of components detected. The output chromatogramis shown in Fig 1 below:
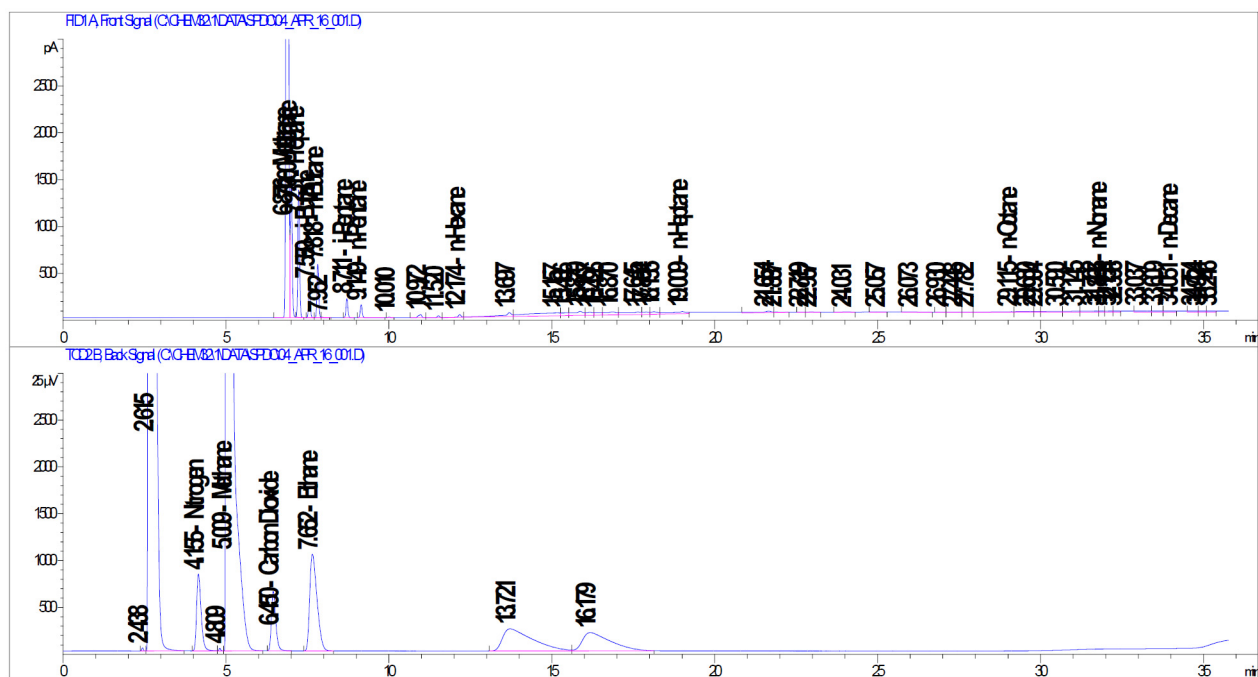
Figure 1—Extract of typical Chromatogram of analyzed gas sample.

Identification of the gas components were carried out using the Agilent chem-station software using retention times and peak area of the components as basis. Quantification of the components in Mol%, from which Condensable hydrocarbon were further calculated in GPM C_{3+} using Microsoft Excel. Table1 and Table 2 found in the Appendix are extracts of some natural gas sample compositions used in this exercise.

On-Site Measurementof Hdp

Cleaned, vacuumed gas cylinder with pressure gauge and steel tubing connected to the dew point tester and liquid nitrogen were all connected to the chosen flowline outlet. The connection was flushed with flowline sample severally and vented into a water container. The analyst meticulously monitored the mirror surface of the dew point tester to ascertain the onset of hydrocarbon film formation. The temperature at which the initial film formation was noticed was recorded as the HDP. Then the process was repeated and average temperature was reported.

Result Quantification

Integrated result of analyzed flare gas sample was exported to Ms Excel sheet. Monthly generated response factor and gas physical properties were already programmed in this Excel sheet; the exported

peak areas were inputted. Response factor which was the calibration factor, served as correction factor for detection discrimination. The mol% of each component was generated by multiplying each peak area by its respective response factor. This was done in triplicate for the three runs of each sample and the average mol% was used to generate analysis statistical uncertainty. GPM of the calculated mol% was further generated by substituting in equation 1:

$$((0.3155 \times (\text{Pure Component Mol. Wt} \times \text{Pure component Gravity})) / 100 \qquad 1$$

The final analysis report was reported at 95% confidence level, which was in tandem with NIST 1297 procedure for measurement uncertainty at the above stated percentage.

Quality Assurance (QA) & Quality Check (QC) Measures

These are those measures put in place to ensure sample integrity is intact; guarantees an analytical instrument perform within acceptable limits and give room for dependable and accurate results. The whole of this exercise was carried out in line with ISO certified standard operating procedure. QA & QC involves sample validation and method validation approaches;

Sample Validation
Gas cylinders were properly washed with solvent, dried with compressed air and vacuumed. During sampling, liners and gas cylinders were purged with the intended sample before collection of samples for analysis.

Duplicate samples from same source were collected. The collected samples were properly labelled and tagged before departure from field. Injection path was flushed with the intended sample for analysis.

Opening pressure check was done on the sample before analysis.

Method Validation

i.   Blank run was done before commencement of analysis.
ii. Calibration: Prior to sample analysis, Standard gas sample was analyzed and computed to generate response factor. The response factor was thus used to calculate the mole percent of the unknown gas samples.
iii. Replicate Test: Duplicate samples were analyzed at same condition to estimate instrument reproducibility.
iv. Precision and Accuracy determination: Standard gas sample was run severally, computed and result generated was compared with certificate of calibration then the deviation was established. Uncertainty in measurement determination was done. Several runs were made on samples and their standard deviations were calculated.
v.   Dehydrated and pure support gases were used.

Results and Discussion

The calculated GPM C_{3+} was plotted against the measured HDP of each gas sample. This was done for all the flow stations. It was gathered from the graph that GPM C_{3+} of associated gases were higher than that of non-associated gases and same applied to their high and low HDP respectively. Fig 2 and Fig 3 are the graphs of HDP and that of their GPM C_{3+} of some analyzed gas samples.
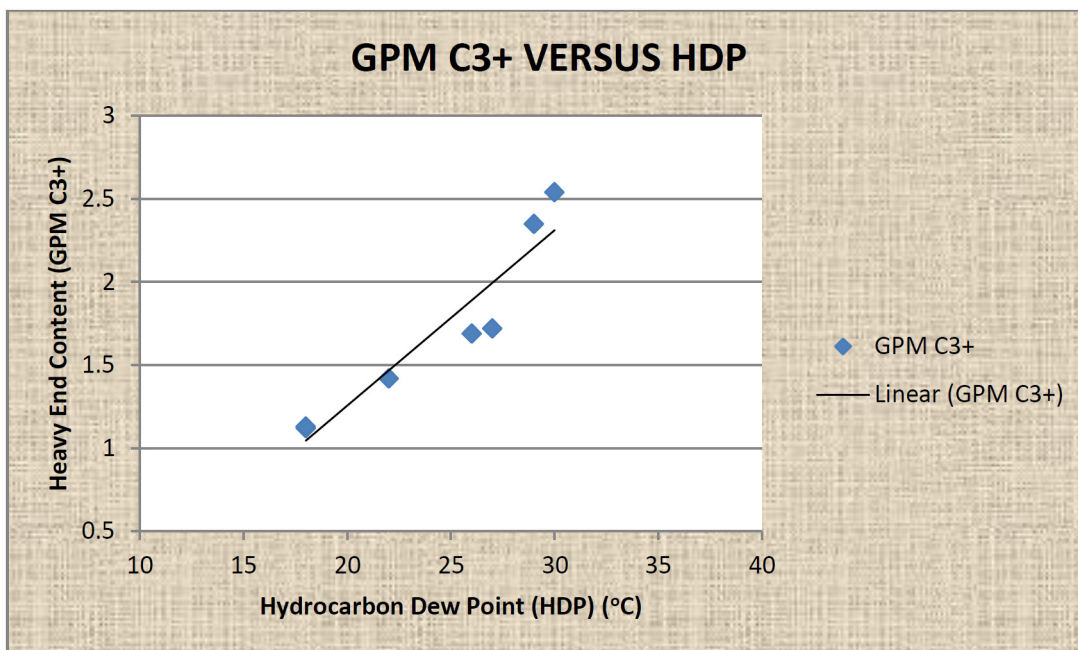
Figure 2—PLOT OF ASSOCIATED GAS HDP WITH GPM C_{3+}
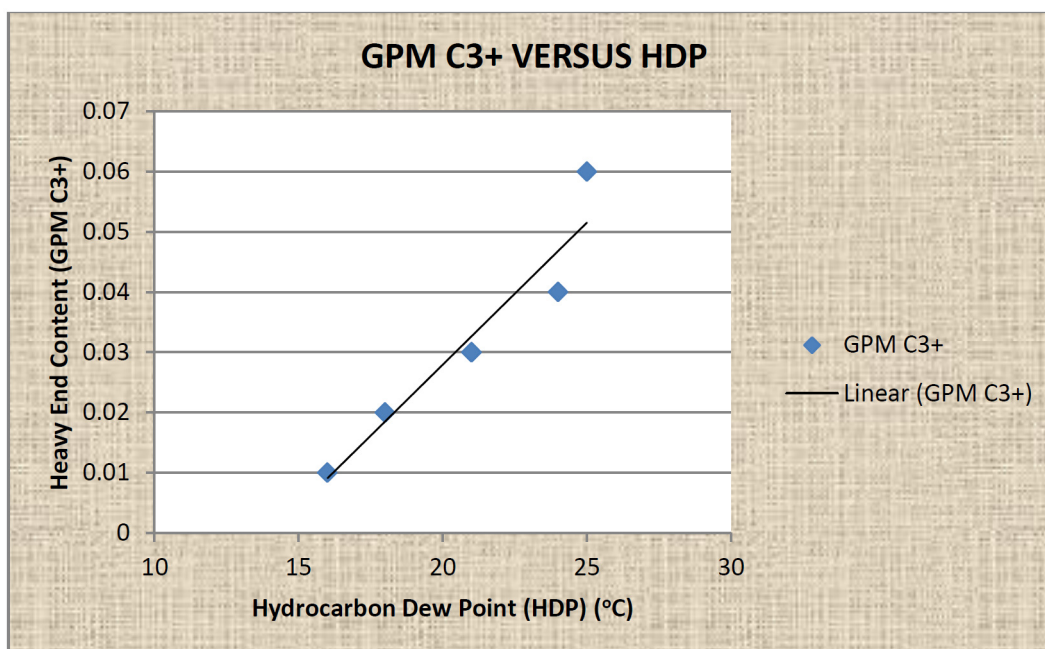
Figure 3—PLOT OF NON- ASSOCIATED GAS HDP WITH GPM $_{C3}$+

From Fig 2 and Fig 3, it was observed that increase in calculated condensable heavy ends also showed increase in HDP and vice versa.

Conclusion

From this work, it can be seen that the measured hydrocarbon dew point can be evaluated with the compositional analysis of the heavy-ends hydrocarbons. Considering the challenging condition surrounding measurement of HDP using manual /visual dew scope, it's necessary to have a back-up basis to scrutinize experimental data, in which GPM C_{3+} is suitable. The implication of employing this heavy

hydrocarbons compositions is to give a practical insight of how the prevailing compositions affects the resultant HDP, ratherthan using fixed ratios of lump heavy ends fractions.

To have a robust confidence in the measured data, necessary quality measures like the following were done: sample validation and method validation in reference with appropriate standards. The confidence level of all generated data was established using statistical evaluation.

Although, the dew-scope approach has been certified by recognized international standard bodies, use of the proportion of the heavy-end compositions should be employed as a double-check method and as a way of evaluating the output from the dewscope instrument.

The chromatographic analysis of the natural gas sample from the gas process facilities in Niger Delta Region, showed that HDP increase with GPM C_{3+} compositions.

It is worth mentioning, that this work didn't pinpoint the exact amount of condensable liquid that will give a particular HDP for any given natural gas sample. Also the impact of flowline conditions other than the time of sampling was not considered.

Recommedation

In a bid to achieve dependable and accurate HDP, it's cogent to quality-check the in-situ experimentally generated result with other approaches. Using the calculated quantity of condensable hydrocarbon components in such natural gas sample promises to be a comparative option.

More research work should be carried out with other HDP measurement approaches in relation with GPM C_{3+}, to test level of compliance with the trend established here.

Acknowledgement

References

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Appendix

Table 1—Non-Associated Gas Composition

Components	Mol.Wt	Gravity	Mol%						Average Uncertaintity
Nitrogen	28.013	0.809	0.05	0.05	0.09	0.38	0.10	0.10	0.02
Carbon Dioxide	44.010	0.818	0.19	0.14	0.15	0.81	0.18	0.19	0.04
Methane	16.043	0.300	98.70	98.91	99.25	98.6	99.00	98.50	0.20
Ethane	30.070	0.356	0.91	0.76	0.47	0.05	0.62	1.07	0.02
Propane	44.097	0.507	0.08	0.07	0.02	0.04	0.03	0.06	0.02
I-butane	58.124	0.563	0.01	0.01	0.01	0.03	0.01	0.01	0.04
N-butane	58.124	0.584	0.01	0.01	0.01	0.02	0.01	0.01	0.02
Iso pentane	72.151	0.625	0.01	0.01	0.00	0.01	0.01	0.01	0.02
N-pentane	72.151	0.631	0.01	0.01	0.00	0.01	0.01	0.01	0.02
Hexanes	84.000	0.690	0.01	0.01	0.00	0.01	0.01	0.01	0.02
Heptanes	96.000	0.727	0.01	0.01	0.00	0.01	0.01	0.01	0.02
Octanes	107.000	0.749	0.01	0.01	0.00	0.01	0.01	0.02	0.01
Nonanes	121.000	0.768	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Decanes	134.000	0.782	0.00	0.00	0.00	0.01	0.00	0.00	0.01
Total			100.00	100.00	100.00	100.00	100.00	100.00	

Table 2—Associated Gas Composition

Components	Mol.Wt	Gravity	Mol%						Average Uncertaintity
Nitrogen	28.013	0.809	0.92	0.03	0.16	0.07	0.05	0.03	0.01
Carbon Dioxide	44.010	0.818	0.54	1.48	17.44	0.74	0.59	0.02	0.02
Methane	16.043	0.300	94.23	91.08	72.86	84.07	87.83	90.75	0.24
Ethane	30.070	0.356	3.83	3.42	4.05	6.55	6.07	4.28	0.02
Propane	44.097	0.507	0.12	2.25	2.58	5.44	3.06	2.49	0.04
I-butane	58.124	0.563	0.13	0.42	0.87	0.93	0.54	0.50	0.01
N-butane	58.124	0.584	0.01	0.73	1.00	1.43	0.99	0.89	0.02
Iso pentane	72.151	0.625	0.07	0.21	0.44	0.26	0.27	0.29	0.02
N-pentane	72.151	0.631	0.00	0.12	0.24	0.23	0.21	0.22	0.01
Hexanes	84.000	0.690	0.08	0.11	0.15	0.14	0.17	0.20	0.01
Heptanes	96.000	0.727	0.04	0.08	0.11	0.10	0.13	0.22	0.00
Octanes	107.000	0.749	0.02	0.05	0.07	0.04	0.09	0.11	0.00
Nonanes	121.000	0.768	0.01	0.02	0.02	0.00	0.00	0.00	0.01
Decanes	134.000	0.782	0.00	0.00	0.01	0.00	0.00	0.00	0.01
Total			100.00	100.00	100.00	100.00	100.00	100.00	