Peng-Robinson Equation of State Natural Gas Dew Points

KENNETH E. STARLING, Ph.D., President, Starling Associates, Inc., Norman, OK

Abstract

A method is presented for accurate calculations of dew points of natural gases in operating gas pipelines. From a typical gas chromatographic analysis coupled with a single chilled mirror or other dew point temperature measurement at pipeline pressure, the gas analysis is extended mathematically so the Peng-Robinson equation of state will match the single measured dew point. The resultant extended analysis then can be used with confidence of acceptable accuracy even when the flowing gas composition changes within specified tolerance limits. The benefit to the industry of this method is the fact that the extreme accuracy required for the use of an extended analysis chromatogram alone is avoided.

Introduction

The focus of this paper is on the need for a reliable method for accurate calculations of dew points for natural gases in operating gas pipelines. The commonly used three step method of sampling, analysis and calculation can encounter undetected errors at each step. Sampling is difficult, accurate analysis is difficult and the resultant calculations of dew point and/or condensed liquid are uncertain.

The direct measurement of the dew point temperature, for example by the chilled mirror method, circumvents the analysis problem, and if online, some of the error sources from sampling to offline containers. The investigation by Warner, et al. (1) indicated that for the natural gases studied, the manual chilled mirror dew point temperature measurement uncertainty was small, 2.4 F.

Thus, the commonly used three step method provides a gas analysis which allows dew point calculations which are uncertain, while direct measurement has low dew point uncertainty but does not allow calculations.

The method proposed in the present work is to combine the direct measurement of dew point and the gas analysis so that the hexanes plus portion of the gas analysis is adjusted to match the measured dew point. This adjustment of the portion of the gas analysis which has the largest uncertainty yields calculation results in the region of the dew point which have much lower uncertainty than the commonly used three step method.

In this paper discussion is first presented related to the commonly used three step method, then the proposed method is presented.

The Three Step Method

The commonly used three step method consists of sampling, analysis and calculation. Obtaining a truly representative sample of the natural gas flowing in the operating pipeline is very difficult. Valuable information regarding sampling is provided in the American Petroleum Institute Manual of Petroleum Measurement Standards, Chapter 14, Section 1 (2). However, sampling is far from an exact science and the API 14.1 Working Group is continuing its research to improve sampling techniques. Even if it were possible to obtain a truly representative sample of the natural gas in the pipeline, the determination of the composition of the sample obtained is very difficult.

Handling the container holding the sample is an issue due to the potential for adsorption and/or condensation, so that the gas which is introduced into analysis equipment may not truly be the composition of the sample which entered the sample container from the pipeline. Then, the composition for the natural gas determined using the analysis equipment may not be sufficiently detailed or accurate for effective use in the more accurate dew point calculation methods. For example, consider a natural gas chromatography analysis using ASTM D 1945 (3) or GPA Standard 2261 (4) with lumping of components heavier the pentanes into hexanes plus. The calculation of the natural gas relative density and heating value using this gas composition would have only small uncertainties using either AGA Report No. 8 (5) or GPA Standard 2172 (6) calculation methods but the calculation of dew point for the natural gas at pipeline pressure by any equation of state would have large uncertainty.

The extended natural gas chromatography analysis method GPA 2286 (7) can be used to identify naphthene and aromatic components and extend the analysis to about hexadecanes. Unfortunately, as has been pointed out by Warner, et al., GPA 2286 extended analysis results for the same natural gas performed by seven different laboratories yielded calculated dew point temperatures spanning a large range, over 100 F. Warner, et al., report an expected uncertainty in the dew point calculated by this method of 33.9 F. In fact, for the third step in the sequence of sampling, analysis and calculation, the uncertainties of equation of state calculations are not well established due to the dearth of accurate experimental dew point data for natural gases of known, highly accurate composition through hexadecanes.

Direct Measurement of Dew Point

Given the uncertainties involved in the commonly used three step method of sampling, analysis and calculation, Warner, et al. have recommended that a practical operational method for monitoring natural gas dew points for operating pipelines is to measure the dew point experimentally using the chilled mirror method, the method pioneered by the Bureau of Mines. According to Warner, et al., repeat measurements by eight different individuals indicated that for the natural gases studied, the chilled mirror dew point temperature measurement uncertainty was less than 2.4 F. Although the recommendation by Warner, et al. appears to provide a practical operational method for monitoring the natural gas dew point for an operating pipeline, it would be advantageous to have in addition a reliable method for accurate calculations of dew points and other properties of the natural gas at other operating conditions. Such a method is presented in this paper.

Philosophy of Proposed Method

The method presented in this paper for accurate calculations of dew points of natural gases in operating gas pipelines is based on the following arguments. First, it is argued that a natural gas can be characterized reasonably in the region of pipeline operations from a typical gas chromatographic analysis with lumping of hexanes plus, coupled with a single chilled mirror or other dew point temperature measurement at pipeline pressure. The key to this characterization of the natural gas is the extension of the gas analysis from chromatography to hydrocarbons of sufficiently high molecular weight to accurately reproduce the measured dew point using an equation of state which is capable of describing the phase behavior of the natural gas. . It then is argued that the resultant extended analysis can be used with confidence of acceptable accuracy even when the flowing gas composition changes within specified tolerance limits.

A number of extended analysis equations have been proposed for modeling the composition versus molecular weight behavior of naturally occurring natural gases, gas condensates and crude oils (8,9). When only two quantities are to be used to characterize the hexanes plus component distribution, a relatively simple equation must be used. In the present work, a two-constant exponential decay curve for heavy component mole fraction versus molecular weight will be used.

There are numerous equations of state which can be used to match the measured dew point, including the BWRS, SRK and Peng-Robinson equations (10,11,12). The Peng-Robinson equation of state will be used in this paper. A major benefit to the industry of this method is the fact that it avoids the need for an experimentally measured extended analysis having the extreme accuracy required for accurate calculations of dew points.

It should be noted that a measured dew point temperature which is less than the pipeline temperature indicates that the gas measured in the dew point equipment would be superheated and therefore single phase gas at the pipeline condition. On the other hand, a measured dew point temperature which is equal to or greater than the pipeline temperature indicates that the composition measured in the dew point equipment would be saturated or subcooled and therefore two phase at the pipeline condition. Thus, considering the uncertainties of maintaining the integrity of a two phase stream, only if the measured dew point temperature is less than the pipeline temperature can the gas measured in the dew point equipment be considered to reliably represent the gas in the pipeline.

Literature Data

For the purposes of this paper, the data reported by Derks, et al. are very useful (13). Derks, et al. present data for the amount of liquid condensed at several temperatures near the dew point at 594.7 psia (4.1 MPa) for two natural gases (Gas A and Gas B). The data for liquid condensed is reported in the units of milligrams of liquid per cubic meter of gas (for gas at 0.0 C temperature and 1.0 standard atmosphere pressure, a gas condition referred to as normal conditions in the Netherlands, where the measurements were made). This quantity is called the Potential Hydrocarbon Liquid Condensed (PHLC). For the natural gas under consideration, the PHLC is the quantity of liquid which would be expected to condense in the pipeline when the flowing temperature drops below the dew point temperature.

Derks, et al. present detailed analyses which include naphthene and aromatic components and which extend to hexadecanes for Gas A and dodecanes for Gas B. The detailed analysis compositions for Gas A and Gas B are given in Table 1, with lumping of helium in nitrogen and neopentane and cyclopentane in isopentane.

Table 1. Gas A and Gas B Detailed Analyses

COMPONENT	GAS A MOL %	GAS B MOL %
NITROGEN	14.345378	2.493194
CARBON DIOXIDE	0.987157	20.513254
METHANE	81.224596	73.520647
ETHANE	2.804993	2.729901
PROPANE	0.392399	0.433971
ISO-BUTANE	0.064715	0.078538
N-BUTANE	0.069674	0.078319
ISO-PENTANE	0.026239	0.035912
N-PENTANE	0.017671	0.021629
HEXANES	0.020883	0.026942
HEPTANES	0.008911	0.013422
OCTANES	0.005522	0.006540
NONANES	0.004160	0.003144
DECANES	0.001804	0.000537
C11S	0.000573	0.000064
C12S	0.000158	0.000011
BENZENE	0.015437	0.025702
CYCLOHEXANE	0.003847	0.006776
MC HEXANE	0.002504	0.006984
TOLUENE	0.003316	0.004511
C13S	0.000045	0
C14S	0.000013	0
C15S	0.000002	0
C16S	0.000001	0
C17S	0	0

Derks, et al. tested the accuracy of the Peng-Robinson equation of state for prediction of the equilibrium temperature at the experimental values of PHLC for Gas A and Gas B and found that the predicted equilibrium temperatures were high.

Equation of State

The Peng-Robinson equation of state in its original form was used in the work in this paper (12). The binary interaction parameters presented by Sandler (14) have been used, with interpolations and extrapolations for some component pairs. Using the detailed analyses presented by Derks, et al., the author's Peng-Robinson equation of state software yields the plots of experimental and predicted PHLC versus temperature for Gas A and Gas B shown in Figures 1 and 2.

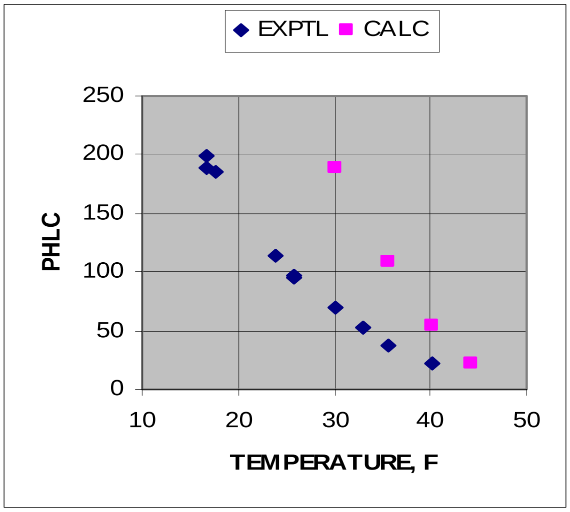

Figure 1. Gas A Detailed Composition PHLC

The predicted curves have the same general shape as the experimental curves but are displaced by a fairly constant temperature difference, as was noted also by Derks, et al.. The curves for Gas A in Figure 1 suggest that if the mole percentages of the components in the hexanes plus portion of Gas A were adjusted, the predictions could be made to match the experimental PHLC curve near the dew point. A similar observation can be made for the curves for Gas B in Figure 2.

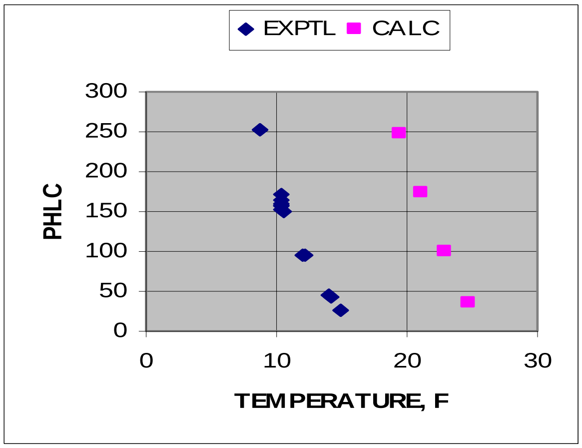

Figure 2. Gas B Detailed Composition PHLC

Hexanes Plus Distribution

The extended analysis equation used in this paper is the following two-constant exponential decay curve for heavy component mole fraction versus molecular weight.

$$Zi/ZC6+ = A\exp(-BMWi) \qquad (1)$$

In Equation (1) Zi is the mole fraction of the ith component, ZC6+ is the experimentally measured hexanes plus mole fraction and MWi is the molecular weight of the ith component. The component molecular weights used in Equation (1) are the normal paraffin hydrocarbon molecular weights. The constants A and B are determined by two requirements. (1) The sum of the calculated mole fractions of the components in the hexanes plus fraction are required to equal the experimentally measured hexanes plus mole fraction, ZC6+. (2) The sum of the calculated mole fractions of the components in the hexanes plus fraction times their molecular weights are required to equal the experimentally measured hexanes plus mole fraction times an assumed trial hexanes plus molecular weight. When the assumed hexanes plus molecular weight yields a calculated dew point in agreement with the experimentally measured dew point, the assumed hexanes plus molecular weight is accepted as characterizing the natural gas and the component distribution from Equation (1) is fixed.

Note that the feasibility of using the distribution in Equation (1) can be evaluated for Gas A and Gas B by plotting the natural logarithm of the component mole fractions Zi versus the component molecular weights MWi. This plot should yield a nearly straight line if Equation (1) is to reasonably represent the hexanes plus component distribution. Figures 3 and 4 show that nearly straight lines result for both Gas A and Gas B.

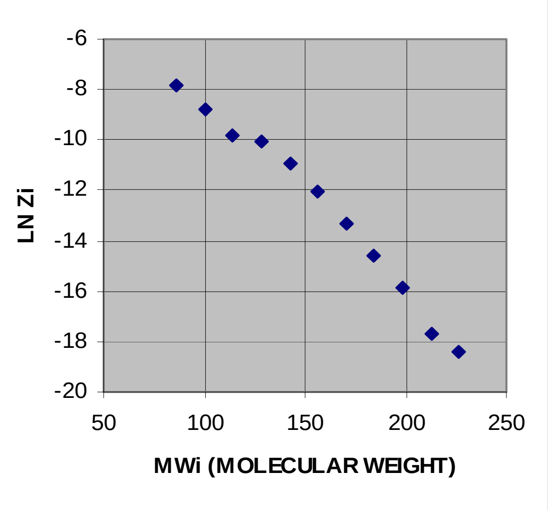

Figure 3. Gas A Logarithmic Distribution

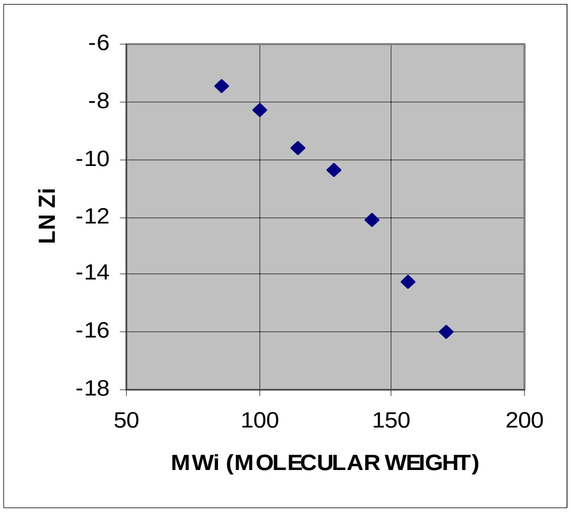

Figure 4. Gas B Logarithmic Distribution

When the mole percentages of the components in the hexanes plus portions of Gas A and Gas B were adjusted to be only normal paraffin hydrocarbons and the distribution for mole percent versus molecular weight was obtained from Equation (1), the results shown in Tables 2 and 3 and Figures 5 and 6 were obtained.

Table 2. Gas A Hexanes Plus Distribution

COMPONENT	EXPTL MOL %	CALC MOL %
C6s	0.040168	0.040704
C7s	0.014731	0.016041
C8s	0.005522	0.006321
C9s	0.004160	0.002491
C10s	0.001804	0.000982
C11s	0.000573	0.000387
C12s	0.000158	0.000152
C13s	0.000045	0.000060
C14s	0.000013	0.000024
C15s	0.000002	0.000009
C16s	0.000001	0.000004
C17s	0.000000	0.000001
HEXANES PLUS	0.067177	0.067176

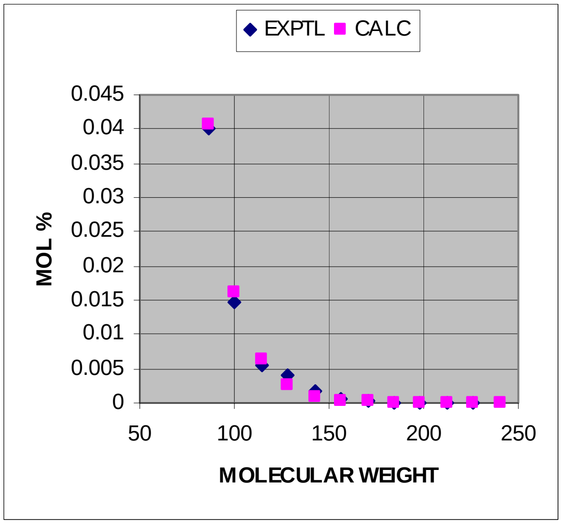

Figure 5. Gas A Hexanes Plus Distribution

. It can be noted for Gas A that the calculated mole percentages reasonably model the mole percentages of experimentally measured components. The adjusted hexanes plus distribution for Gas A in Table 2 has a molecular weight of 95.3, compared with the experimental hexanes plus molecular weight of 94.1. Using the compositions in the adjusted hexanes plus distribution, the Gas A calculated dew point temperature is 52.1 F.

Table 3. Gas B Hexanes Plus Distribution

COMPONENT	EXPTL MOL %	CALC MOL %
C6s	0.059421	0.070160
C7s	0.024918	0.018145
C8s	0.006540	0.004692
C9s	0.003144	0.001214
C10s	0.000537	0.000314
C11s	0.000064	0.000081
C12s	0.000011	0.000021
C13s	0.000000	0.000005
C14s	0.000000	0.000001
HEXANES PLUS	0.094634	0.094634

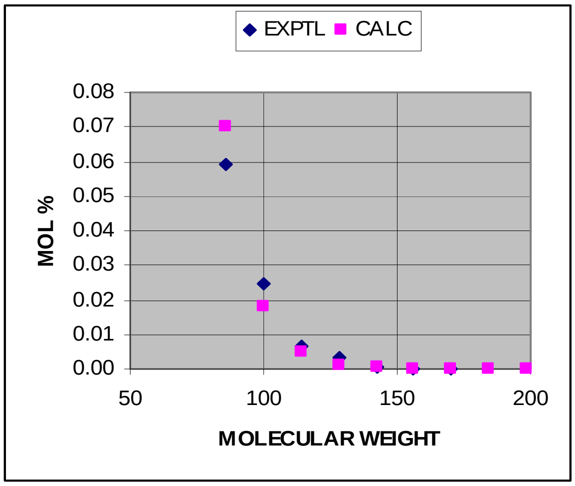

Figure 6. Gas B Hexanes Plus Distribution

For Gas B, the adjusted hexanes plus distribution in Table 3 has a molecular weight of 91.1, compared with the experimental hexanes plus molecular weight of 90.7. Using the compositions in the adjusted hexanes plus distribution, the Gas B calculated dew point temperature is 18.6 F.

Predicted PHLC Versus Temperature

The Peng-Robinson equation of state calculations of PHLC versus temperature are shown in Figures 7 and 8.

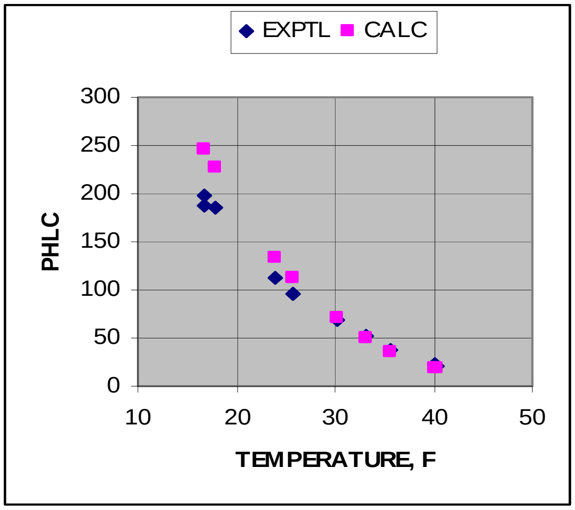

Figure 7. Gas A Adjusted Composition PHLC

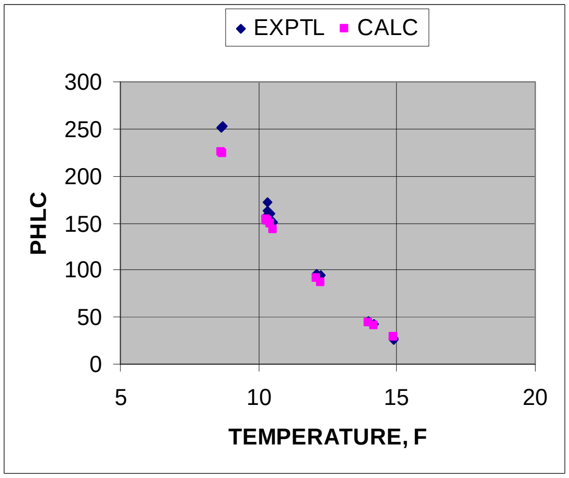

Figure 8. Gas B Adjusted Composition PHLC

Experimental dew points for Gas A and Gas B were not reported by Derks, et al. Nevertheless, the close agreement of the calculated and experimental PHLC values near the dew points in Figures 7 and 8 indicates that with the adjusted hexanes plus molecular weight values selected, the calculated dew point temperatures have uncertainties similar to the 2.4 F measurement uncertainty reported by Warner, et al.

Based on these results, it is clear that if an adjusted hexanes plus component distribution is used such that the Peng-Robinson equation of state reproduces the natural gas dew point, then the condensation behavior predicted near the dew point can be expected to be reasonably accurate. In particular, when only a gas chromatography analysis lumping components heavier than pentanes into hexanes plus is available, Equation (1), which reasonably models the composition versus molecular weight behavior of natural gases, can be used to determine a hexanes plus molecular weight which matches a measured dew point.

Estimate of Uncertainty of Method

There are two cases in which the uncertainty of a calculated pipeline natural gas dew point temperature will be estimated here. The first case is the initial condition when both the gas analysis and the dew point have just been measured and the extended analysis for the hexanes plus has been determined. In this case, the adjusted gas analysis perfectly matches the measured dew point temperature, so that the uncertainty in the calculated dew point temperature equals the uncertainty in the measured dew point temperature. Warner, et al. (REF) report that using a manual chilled mirror dewscope, measured natural gas dew point temperatures have an uncertainty of 2.4 F provided the ambient temperature is greater than the gas dew point temperature.

The second case is a later condition when a new gas analysis is to be used to calculate the dew point using the hexanes plus component distribution determined earlier from the measured dew point temperature. In this case, the uncertainty in the calculated dew point is due to a combination of the uncertainty in the gas analysis and the uncertainty in distribution in the components in the hexanes plus portion of the gas. When the dew point measurement has not been repeated, it is possible to evaluate only calculation uncertainty due to the uncertainty in the gas analysis. The American Society for Testing Materials in its standard, ASTM D 1945, provides the following criteria for precision (REF). For duplicate measurements from the same chromatographic analysis equipment, duplicate measurements for a mol % of 0.0 to 0.1 should be considered suspect (possibly in error) if they differ by more than 0.01 mol %.

To determine the sensitivity of the calculated dew points for Gas A and Gas B due to the uncertainty in the hexanes plus portion of the gas analysis, calculations were performed both adding and subtracting 0.01 mol % to the experimental hexanes plus mol %. The results, which are given in Table 4, indicate the uncertainty in calculated dew point due to the uncertainty in the measured hexanes plus mol % depends on the hexanes plus molecular weight. For Gas A, with the adjusted distribution hexanes plus molecular weight of 95.3, the sensitivity is 4.2 F. For Gas B, with has the lower adjusted distribution hexanes plus molecular weight of 91.1, the sensitivity also is lower, 3.2 F.

Table 4. Dew Point Sensitivity to Hexanes Plus

MOL % HEXANES PLUS	CALCULATED DEW POINT, F GAS A	GAS B
ADJUSTED	52.1	18.6
ADJUSTED + 0.01	55.9	21.5
ADJUSTED - 0.01	47.9	15.4

The uncertainty in the calculated dew point due to the combined uncertainty in the measured hexanes plus mol % and the measured dew point temperature therefore is approximately the sum of the two uncertainties, 5.6 F for Gas A and 4.6 F for Gas B. Of course, if the distribution of components in the hexanes plus portion of the gas changes, these uncertainties will be increased.

ASTM D 1945, provides the following criteria for reproducibility. For duplicate chromatographic analyses in two different laboratories, duplicate measurements for a mol % of 0.0 to 0.1 should be considered suspect (possibly in error) if they differ by more than 0.02 mol %. Based on the ASTM D 1945 standard of 0.01 mol %.for repeatability and 0.02 mol % for reproducibility, it seems reasonable to require a repeat measurement of pipeline natural gas dew point temperature in the proposed method when the hexanes plus portion of the gas has changed by 0.01 to 0.02 mol %.

Use in Pipeline Operations

There are numerous possible scenarios for use of the method proposed in this paper in pipeline operations. Applications could vary depending on whether a company is involved in production, field gathering, processing or transmission. Also, the size of the flow in the pipeline and contract requirements can impact the nature of the application.

For a pipeline having both online chromatography and dew point equipment, the method presented in this paper could be applied each time a chromatogram result is output to the data system, using the measured dew point temperature corresponding closest to time the sample analyzed entered the gas chromatograph.

For a pipeline having online chromatography but without online dew point equipment, portable dew point equipment could be used periodically to obtain a measured dew point in order to apply the method. The hexanes plus composition distribution determined using the proposed method then could be used until the next dew point measurement is made. During the interval between dew point measurements the predicted dew point will vary due to changes in the online chromatographic analyses, as discussed in the previous section of this paper. When the predicted dew point uncertainty becomes sufficiently large, a new dew point measurement should be made. The criterion for a new dew point measurement may be made according to company policy or even by contractual agreement.

Conclusions

A method has been proposed in this paper for accurate calculations of dew points of natural gases in operating gas pipelines. From a typical natural gas chromatographic analysis with lumping of components heavier than pentanes into hexanes plus, coupled with a single chilled mirror or other dew point temperature measurement at pipeline pressure, the gas analysis is extended mathematically so the Peng-Robinson equation of state will match the single measured dew point. The resultant extended analysis then can be used with confidence of reasonable accuracy even when the flowing gas composition changes within specified tolerance limits. For pipeline quality natural gases, the estimated uncertainty in the calculated dew point temperature is 5 to 6 F. A potential benefit to the industry of the proposed method is the fact that it has fewer possible sources of undetected errors than the commonly used three step method of sampling, analysis and calculation.

References

1. Warner, H. R., Leamer, E. E., Spence, A. P., Bone, R. L., Hubbard, R. A., Bernos, J., and Kriel, W. A., "Hydrocarbon Dewpoint Determination of Lean Natural Gases," Proceedings, 80th Annual Convention, Gas Processors Association, 2001.

2. Manual of Petroleum Measurement Standards, Chapter 14, Section 1, Collecting and Handling of Natural Gas Samples for Custody Transfer, American Petroleum Institute, 2001.

3. American Society for Testing Materials standard, ASTM D 1945.

4. GPA Standard 2261, Analysis for Natural Gas and Similar Gaseous Mixtures by Gas Chromatography, Gas Processors Association.

5. Starling, K. E. and Savidge, J. L., AGA Transmission Measurement Committee Report No. 8, Compressibility Factors of Natural Gas and Other Related Hydrocarbon Gases, American Gas Association, 1992, Reprint Version, 1994.

6. GPA Standard 2172, Calculation of Gross Heating Value, Relative Density and Compressibility Factor for Natural Gas Mixtures from Compositional Analysis, Gas Processors Association, 1995.

7. GPA Tentative Standard 2286, Tentative Method of Extended Analysis for Natural Gas and Similar Gaseous Mixtures by Temperature Programmed Gas Chromatography, Gas Processors Association.

8. Pederson, K. S., Fredenslund, A. and Thomassen, P., *Properties of Oils and Natural Gases*, Gulf Publishing Company, 1989.

9. Whitson, C. H., "Characterizing Hydrocarbon Plus Fractions," *SPE Journal*, **23**: 683, 1983.

10. Starling, K. E., *Fluid Thermodynamic Behavior for Light Petroleum Systems*, Gulf Publishing Company, 1973.

11. Soave, G., *Chemical Engineering Science*, **27**: 1197, 1972.

12. Peng, D. Y. and Robinson, D. B., *Industrial and Engineering Chemistry Fundamentals*, **15**: 59, 1976.

13. Derks, P. A. H., van der Meulen-Kuijk, L., and Smit, A. L. C., "Detailed Analysis of Natural Gas for an Improved Prediction of Condensation Behavior," Proceedings, 72nd Annual Convention, Gas Processors Association, 1993.

14. Sandler, S. I., *Chemical Engineering Thermodynamics*, Second Edition, John Wiley & Sons, 1989.