# REPORT OF EXPERT CONSULTANT DR. KENNETH E. STARLING ON HYDROCARBON DEW POINT DETERMINATION 2006-11-19

## **EXECUTIVE SUMMARY**

In this project it was required that a recommendation be made for the best of three methods for measurement of the hydrocarbon dew point at the Points of Entry of the National Transport System for natural gas in Colombia, under performance and operability criteria.

Two of the methods considered are manual methods and therefore cannot be utilized for continuous (or even semi-continuous, less than 30 minute) measurements. The ASTM D-1142 method typically requires up to an hour of technician time for a single measurement. The constant composition expansion method requires obtaining a natural gas sample from the pipeline, transporting the sample to the laboratory and up to one day of technician time to make a single measurement. In addition, the constant composition expansion method is not practical near the mixture cricondentherm or for lower dew points or for natural gases having long hydrocarbon tails with high molecular weight components beyond decanes.

Only one of the three methods considered is pragmatic with respect to efficient and economic gas quality control, the CONDUMAX (or CONDUMAX II) method, an online analyzer which makes a dew point measurement approximately every 10 minutes. However, because the CONDUMAX type of device requires calibration, its performance with respect to accuracy is dependent upon the accuracy of the calibration method.

Gasunie Engineering and Technology has developed a highly accurate CONDUMAX II calibration method using their GACOM device. Because the GACOM equipment is not commercially available in Colombia, the less accurate ASTM D-1142 method is recommended for calibration of CONDUMAX and other online analyzers. A more detailed list of conclusions and recommendations is presented at the end of this report.

#### BACKGROUND

This report was prepared by Dr. Kenneth E. Starling, PhD, an expert consultant in the area of Natural Gas Quality. On November 4, 2005, Dr. Starling was contacted by Mr. Alejandro Villalba of Promigas. Mr. Villalba stated that the Colombian natural gas hydrocarbon dew point (HCDP) contracting parties desired that I prepare a proposal as an expert consultant with the objective discussed below. The proposal was prepared and sent to Mr. Villalba on November 11, 2005. This proposal is given in Appendix 1. On January 12, 2006, Dr. Starling was contacted by Mr. Jorge Duran of CREG (Comision de Regulacion de Energia y Gas) stating that CREG would be funding the study. A copy of the proposal was sent to Mr. Duran.

On January 23, 2006 Dr. Starling had a telephone conference meeting with Mr. Jorge Duran of CREG and Mr. Alejandro Villalba of Promigas. Mr. Duran and Mr. Villalba stated that the Colombian natural gas hydrocarbon dew point (HCDP) contracting parties desired that I prepare a statement of the information that I would like to have regarding sampling and analysis for the three natural gases to be sampled. This document, titled **REQUEST FOR SAMPLING**, **ANALYSIS INFORMATION FROM CONSULTANT DR. KENNETH E. STARLING was sent to** Mr. Duran and Mr. Villalba on January 23, 2006. This document is given in Appendix 2. On January 26, 2006, Mr. Duran of CREG sent Dr. Starling the contract for the work. Dr. Starling signed the contract signature page and sent the signature image to Mr. Duran on January 26, 2006.

In the period from January 26, 2006 and September 12, 2006 efforts were in progress to determine the compositions of each of three natural gas samples. Analyses were made at three different laboratories with significantly different results for components with molecular weights greater than pentane. On September 12, 2006 the document titled RECOMMENDED GAS COMPOSITIONS AND PRESSURES FOR HCDP UNCERTAINTY ESTIMATES by Dr. Kenneth E. Starling was sent to Mr. Jorge Duran of CREG. This document is given in Appendix 3. On September 28, 2006 the agreed 60 day period for completion of this report began.

# OBJECTIVE

To evaluate the following three (3) methods for determining the natural gas hydrocarbon dew point in transportation systems:

(1) CONDUMAX hydrocarbon dew point on line analyzer;

(2) Experimental CCE (constant composition expansion) test, based on API RP 44;

(3) Manual determination through the cooled mirror methodology (flat), as per standard ASTM D 1142-95, with a tolerance of more or less 1°C;

and to recommend the best of the three methods for measurement thereof at the Points of Entry of the National Transport System in Colombia, under performance and operability criteria.

The REFERENCES section of this report provides literature references for the CONDUMAX method (1), the API RP 44 document (2) and the ASTM D-1142 method (3).

# SCOPE (Expert Consultant's Comments)

It was proposed by the Expert Consultant Dr. Kenneth E. Starling to perform a technical evaluation to estimate the uncertainty of each method for a range of natural gas compositions and pipeline operating pressures of interest to the contracting parties.

It was requested that three natural gas compositions and three pipeline operating pressures be provided to the Expert Consultant Dr. Kenneth E. Starling to perform a technical evaluation to estimate the uncertainty of each method at each condition. This evaluation exercise involves 27 uncertainty estimations (3 methods times 3 compositions times 3 pressures).

I stated in my proposal that I wished to evaluate the CONDUMAX II, not earlier versions. I believe that the CONDUMAX II has received a valid test by Gasunie. This opinion is based on my meetings and correspondence with Mr. Henk Jan Panneman of Gasunie and Mr. Arthur Scheffer, Mr. Andy Benton and Mr. Andrew Stokes of Michell Instruments, the CONDUMAX II manufacturer, in regard to the Gasunie evaluation of CONDUMAX II using the Gasunie Automatic Condensation Meter, GACOM. It is my understanding that CONDUMAX and CONDUMAX II are sufficiently similar that the conclusions of this study should apply to either instrument.

For the constant composition expansion test, I stated in my proposal that I wished to evaluate the ACB constant composition expansion equipment and test method, because I have previously studied this method in detail with the cooperation of Core Laboratories and information from the equipment manufacturer. The ACB equipment, manufactured in France, was designed specifically for constant composition expansion tests and therefore I believe it is a good choice for evaluation of the constant composition expansion method. However, to provide a literature reference to the constant composition expansion method, please refer to the Sloane type cell discussed in reference (4), Pederson, K. S. Fredenslund, A. and Thomassen, P., "Properties of Oils and Natural Gases," Gulf Publishing Company, 1989.

The manual determination through the cooled mirror methodology (flat), as per standard ASTM D 1142-95 (Bureau of Mines dewscope) is the traditional method for measuring natural gas dew points. I stated in my proposal that I have done a lot of unpublished work in analyzing how the Bureau of Mines dewscope operates and why different uncertainties result for different gas compositions and different pressures. This unpublished work is in reasonable agreement with published literature which is referred to in this report.

### DELIVERABLES

Recommend an industry accepted international methodology to determine the hydrocarbon dew point at the Point of Entry of the National Transport System. This recommendation will be supported by a written report and an executive presentation to the contracting parties. This written report, referred to as the final report, is the present document.

Deliver as part of the final report an interpretation of the recommended methodology's technical basis, according to standards and practices recognized internationally.

Deliver as part of the final report critical aspects found and recommendations for avoiding problems.

## **EXECUTION SITE (Expert Consultant's Comments)**

The work performed in this project by the Expert Consultant Dr. Kenneth E. Starling was carried out in the United States of America except for a trip to Bogota, Colombia for an executive presentation to the contracting parties.

## **EXECUTION TIME (Expert Consultant's Comments)**

The contract states that the contract will last 60 calendar days since the reception, by the Consultant, of the information given by the Transporters and Producers. The contract will not go beyond December 31, 2006.

The information to be given by the Transporters and Producers is the information requested in the document titled REQUEST FOR SAMPLING, ANALYSIS INFORMATION FROM CONSULTANT DR. KENNETH E. STARLING. The text of this document is presented in Appendix 2.

# HCDP PRESSURES USED IN PROJECT

As noted in the proposal scope, three natural gas compositions and three pipeline operating pressures were to be provided to the Expert Consultant Dr. Kenneth E. Starling to perform a technical evaluation to estimate the uncertainty of each method at each condition.

It can be noted in Appendix 3 that the following pressures were recommended by the Expert Consultant Dr. Kenneth E. Starling: 1025 psia, 615 psia and 415 psia. These recommended pressures are based on the objectives discussed below.

First, it is reasonable to make uncertainty estimates at a typical transmission pipeline operating pressure. The pressure of 1025 psia is near the pipeline pressures at the sample points for both the Ballena-Barranquilla-Cartagena (BBC) gas sample and the Ballena-

Barrancabermeja (BB) gas sample. The pipeline pressure at the sample point for the Cusiana gas sample is 1212 psia, which is too close to the cricondenbar pressure for this gas (above the cricondenbar pressure, the gas remains one phase at all temperatures of practical interest).

Second, it is reasonable to make uncertainty estimates at pressures near the pressure where the maximum dew point temperature is expected to occur (the cricondentherm temperature). For both the Ballena-Barranquilla-Cartagena (BBC) gas sample and the Ballena-Barrancabermeja (BB) gas sample, the cricondentherm pressure is expected to be near 415 psia. For the Cuisiana gas sample, the cricondentherm pressure is expected to be near 615 psia.

## GAS COMPOSITIONS USED IN PROJECT

Chromatographic analyses from three laboratories for each of three natural gas pipeline mixtures have been provided by CREG to Dr. Starling. The three laboratories are Instituto Colombiano del Petroleo (ICP), Core Laboratories Venezuela (CLV) and Core Laboratories Aberdeen (CLA). There is generally good agreement between laboratories for nitrogen, carbon dioxide and the hydrocarbons with 1 to 5 carbon atoms. The agreement between laboratories for hydrocarbons with 6 or more carbon atoms (hexanes plus or C6+) is generally not good.

Because the C6+ hydrocarbons have large influences on the HCDP (hydrocarbon dew point) and the amount of liquid condensed near the HCDP, additional information must be introduced to insure that the compositions used in the project yield predicted behavior in close approximation to the behavior experienced in actual field or processing operations.

The methods used for determining the compositions of the three natural gases are discussed in the document in Appendix 3 titled RECOMMENDED GAS COMPOSITIONS AND PRESSURES FOR HCDP UNCERTAINTY ESTIMATES. The compositions used are given in Table 1.

Table 1. Gas Compositions used in this Re
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	BBC Gas	BB Gas	Cusiana Gas
COMPONENT	Mole%	Mole%	Mole%
N2	1.452883	1.542639	0.612190
CO2	0.167219	0.082357	1.847474
H2S	0.000000	0.000000	0.000000
C1	98.037947	98.029840	82.891012
C2	0.225034	0.237832	9.861376
C3	0.056400	0.053460	3.499574
IC4	0.022475	0.017539	0.511360
NC4	0.008760	0.008925	0.548156
IC5	0.010148	0.008402	0.133198
NC5	0.002445	0.002301	0.091328
C6	0.002574	0.002126	0.002668
C7	0.002039	0.001640	0.000297
C8	0.003605	0.003641	0.000131
C9	0.002099	0.002095	0.00008
C10	0.001358	0.001543	0.00006
C11	0.001115	0.001115	0.000000
C12	0.000558	0.000558	0.000000
M-CYCLO-C5	0.000754	0.000907	0.000597
BENZENE	0.000031	0.000352	0.000134
CYCLO-C6	0.000322	0.000443	0.000276
M-CYCLO-C6	0.000809	0.000680	0.000042
TOLUENE	0.000267	0.000488	0.000172
M-XYLENE	0.000632	0.000580	0.000005
O+P-XYLENE	0.000051	0.000051	0.000000
C13	0.000279	0.000279	0.000000
C14	0.000139	0.000139	0.000000
C15	0.000070	0.000070	0.000000

The Cusiana gas is processed before it undergoes custody transfer and enters the gas transmission pipeline. Because the conditions at the last vapor-liquid separation point are known, these conditions can be used to adjust the mole% (mole percentage) values for the highest carbon number components and perhaps extend the number of components slightly for improved consistency with the known conditions. The method used was to start with the average Cusiana gas composition discussed in Appendix 3 and use the Peng-Robinson equation of state (PR EOS) to perform a flash calculation at the separator condition of 0.0 F (Fahrenheit) and 1015 psia. This calculation yielded approximately 2 lb-moles of liquid per lb-mole of mixture, indicating the C6+ mol% was too large for consistency with a dew point at the separator condition. Therefore, the C6+ mol% was reduced to the amount in Table 1 to match the dew point at the separator condition.

Because the Guajira gas is produced from a non-associated reservoir and the gas does not undergo hydrocarbon processing, it is not possible to adjust the composition using an operating condition. However, Mr. Alejandro Villalba of Promigas has provided Condumax sensitivity calibration data, along with chromatographic analyses for three separate days of operation of the Ballena-Barranquilla-Cartagena (BBC) gas pipeline. The average C6+ mole% from these three analyses is 0.0167 mole%. To be consistent with these Condumax data, the C6+ mole% of the gas should be 0.0167 mole%. This adjustment is discussed in Appendix 3.

It also is known that low temperature distillations of samples of Guajira gas indicate the presence of hydrocarbons up to pentadecanes. For this reason, a small amount of C11+ extending to pentadecanes (0.00216 mol%) was included in the Ballena-Barranquilla-Cartagena (BBC) gas and the Ballena-Barrancabermeja (BB) gas compositions given in Table 1. This mol% of C11+, which is smaller than the average mol% of C11+ from the low temperature distillations, provides a condensation profile which is reasonably consistent with the Condumax sensitivity calibration data for the Ballena-Barranquilla-Cartagena (BBC) gas provided by Mr. Villalba. Because the Guajira gas does not undergo hydrocarbon processing and because glycol dehydration is not expected to remove all of the C11+, this small amount of C11+ (0.00216 mol%) seems reasonable.

### **HCDP EQUIPMENT PROCESSES**

The hydrocarbon dew point (HCDP) methods considered in this project are based on detection of liquid condensed near the HCDP. Figure 1 shows a phase envelope for the BBC gas composition in Table 1 estimated using the Peng-Robinson equation of state (PR EOS).

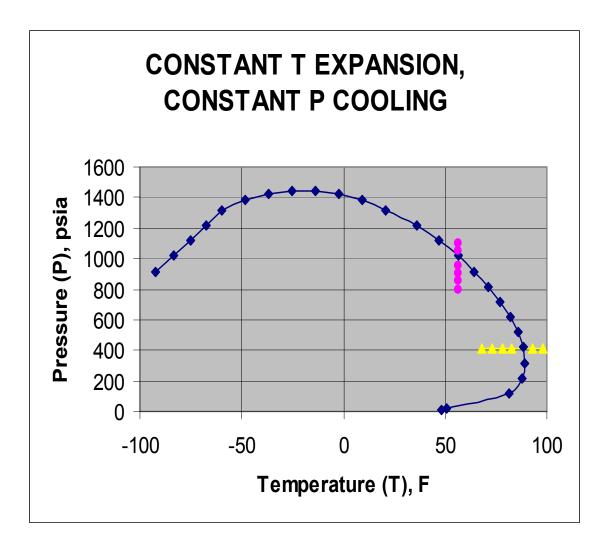


Figure 1. Paths of Constant T Expansion and Constant P Cooling

The points in Figure 1 which form a vertical line correspond to constant temperature expansion of the BBC gas from a pressure above the HCDP to a point inside the two phase region. This is the constant composition expansion (CCE) process. A quantitative record of the condensed liquid volume versus pressure is obtained as the mixture is slowly expanded and these data are extrapolated to zero condensed liquid volume to estimate the HCDP.

The points in Figure 1 which form a horizontal line correspond to constant pressure cooling of the BBC gas from a temperature above the HCDP to a point inside the two phase region. Very approximately, both the ASTM D-1142 method and the CONDUMAX

(or CONDUMAX II) methods follow this horizontal path. However, cooling is supplied only to a cooled mirror and there is no quantitative record of the condensed liquid volume versus temperature. Instead, these methods attempt to detect the presence of condensed liquid on the chilled mirror when the condensed liquid volume is small; the recorded temperature is estimated to be the HCDP. In the ASTM D-1142 method, the light source is natural light and the human eye is used to visually detect liquid on the cooled surface. In the CONDUMAX method (and CONDUMAX II method) the light source is a visible red emitting diode and a photoelectric cell is used to detect liquid on the cooled surface.

#### DISCUSSION OF CCE EQUIPMENT AND METHOD

Discussion is given here of the constant composition expansion (CCE) type of HCDP equipment and operation method. Figure 2 is a scan of the Sloane type cell discussed in reference (4), Pederson, K. S. Fredenslund, A. and Thomassen, P., "Properties of Oils and Natural Gases," Gulf Publishing Company, 1989. I have previously studied this method in detail for the case of the ACB constant composition expansion equipment and test method.

Referring to Figure 2, the mixture is contained in the visual cell by mercury pumped into the bottom of the cell and a piston above the mixture which is moved in position by mercury pumped into the top of the cell using a second mercury pump. The sample volume is large (usually more than 600 cubic centimeters at the dew point in the case of the ACB cell), so the initial formation of liquid visible through the sapphire viewing window does not appreciably change the composition of the remaining gas phase. The entire cell is in a constant temperature enclosure.

The mixture is charged into the cell as a gas at a pressure far above the upper dew point pressure and then is allowed to equilibrate thermally. The initial volume is established by the piston positions of the mercury pumps. The mercury level in the bottom of the cell is maintained at a baseline position within the viewing height of the sapphire viewing window.

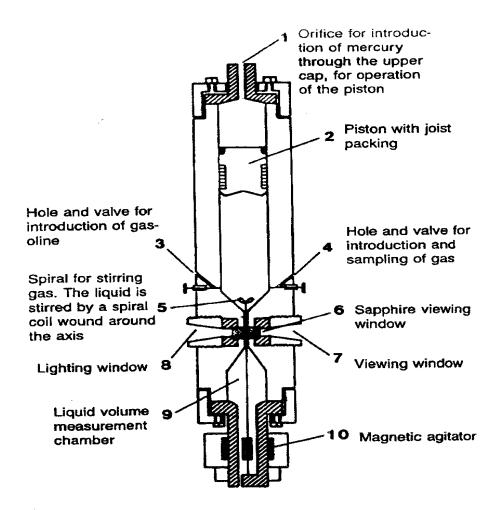


Figure 2. Scan of Sloane Type Cell from Reference (4)

To allow expansion of the gas mixture, mercury is withdrawn from above the piston, while keeping the mercury level in the bottom of the cell at the baseline position. The pressure usually is reduced in increments, with stirring to insure equilibration and equilibrium. When liquid hydrocarbon is first detected visually in the small diameter cell bore at the viewing window, the pressure recorded. The volume of liquid hydrocarbon in the small diameter cell bore at the viewing window is determined from the volume of mercury which must be withdrawn from the bottom of the cell to move the meniscus of the hydrocarbon liquid to the original mercury baseline level. When liquid is initially detected the pressure will be below the true dew point pressure. For this reason, the pressure is further reduced in increments and the volume of condensed liquid is determined at each pressure. The liquid volume percent is then plotted versus pressure and the intersection of this curve with zero volume percent is reported as the liquid volume percent dew point pressure.

Some points to note follow. The Sloane type of dew point equipment was designed for measurement of upper dew point pressure, not lower dew point pressures. The Sloane type of dew point equipment cannot be used effectively at temperatures where the amount of liquid condensed is too small for accurate measurement, such as near the cricondentherm. For natural gas dew point measurement, the Sloane type of dew point equipment is less accurate for unprocessed gases which have long hydrocarbon tails than for processed gases which have had heavy hydrocarbons removed. This is because for natural gases with long hydrocarbon tails, the expansion must be far below the upper dew point pressure before sufficient hydrocarbon liquid has condensed to be detected visually.

From the above discussion, it is concluded that although the constant composition expansion method could be used for accurate measurement for the Cusiana gas composition in Table 1 at 1025 psia, it could not be used at either 615 psia (because condition is too near the cricondentherm) or 415 psia (because condition probably is a lower dew point pressure). With respect to the Guajira gas compositions in Table 1 (BBC and BB), constant composition expansion measurements at 1025 psia or 615 psia, would yield insufficient liquid near the dew point for accurate quantitative measurement due to the effects of the unprocessed gas hydrocarbon tails. Because the dew point temperatures of these gases at 415 psia are near the cricondentherms for these gases, the constant composition expansion method could not be used for measurements at 415 psia.

### DISCUSSION OF ASTM D-1142 EQUIPMENT AND METHOD

Discussion is given here of the ASTM D-1142 type of HCDP equipment and operation method. The basic apparatus has changed

very little since it was developed in the 1930s. Figure 3 is a scan of the apparatus from reference (5), Deaton, W.M. and E.M. Frost, Jr., "Gas Hydrates and Their Relation to the Operation of Natural-Gas Pipe Lines," United States Bureau of Mines Monograph 8, July 1946. A modern version, the Chandler Dewscope, is manufactured by Ametek (<u>www.ametek.com</u>).

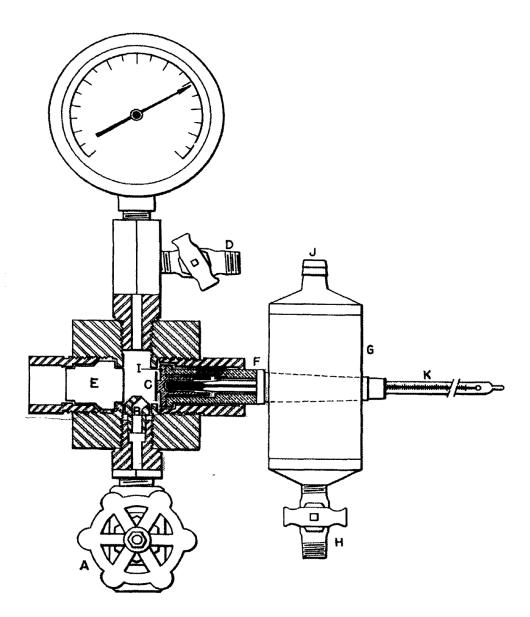


Figure 2. Scan of ASTM D-1142 Equipment from Reference (5)

Cowper (6) has presented a discussion of the cooled mirror method for natural gas hydrocarbon dew point measurements in which he shows a cooled mirror device diagrammatically similar to Figure 4.

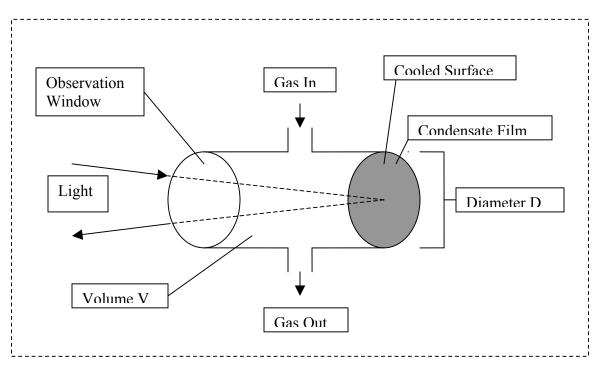


Figure 4. Cooled Mirror Schematic

A common feature of cooled mirror devices such as the ASTM D-1142 device is that liquid condenses from the gas onto the cooled surface and the liquid film must be sufficiently thick for detection. Cowper (6) states that using light with a wavelength of 500 microns (one micron=one millionth of a meter), the amount of liquid which must be condensed on the cooled mirror surface for detection with the human eye corresponds to a liquid thickness equal to the wavelength of the light source. According to Cowper, this amount of liquid corresponds to an estimated 76 mg/Nm3 (76 milligrams of liquid per cubic meter of gas at normal conditions of 0 degrees C and 1 atmosphere pressure) or 0.6 gal/MMscf (0.6 gallons of liquid per million standard cubic feet of gas at 60 degrees F and 14.696 psia).

Cowper states that the fact that a finite volume of liquid must be present for detection implies that the cooled mirror temperature is actually below the true dew point temperature (where liquid starts to condense) and further, the amount of subcooling of the cooled mirror below the true dew point depends on the gas composition and the pressure of measurement.

The analysis by Cowper (6) has the following implied assumptions, (1) a fixed amount of gas is trapped in the equipment, rather than flowing continuously, (2) the temperature measured equals the cooled mirror temperature (no lag), (3) the gas temperature and the condensed liquid temperature are equal, and (4) phase equilibrium exists between the condensed liquid and the vapor in the equipment. Thus, Cowper's analysis should not be considered to be quantitatively accurate, although an experienced operator of the ASTM D-1142 device can reduce the differences in temperatures by utilizing lowered gas flow rates and lowered cooled mirror cooling rates, which also leads to a closer approach to phase equilibrium.

Bergman, et al. (7) have presented a discussion of the ASTM D-1142 method dewscope measurements of natural gas hydrocarbon dew point measurements on pages 34-35 of the AGA project PR 26-69 report. For pipeline gas tests referred to as Willow Run Joint Tests, at 500 psia, the first observation of a faint ring of hydrocarbon condensing occurred at 33 F and droplets were observed at 25 F. Measurements at pressures from 200 to 520 psia exhibited this same type of behavior. Cooling to temperatures below the first observation of droplets resulted in the coalescence of droplets to form a liquid film (referred to as flooding). The authors make the following statement. "One interpretation of this dew point measurement is that the ring approaches the dew point and could be a bit low. The droplet stage might be thought of as 0.3 to 0.5 gallon per MMcf while the flood stage is from 1 to 1.5 gallons per MMcf."

To summarize the implications from Cowper (6) and Bergman, et al. (7), Cowper's analysis indicates that the ASTM D-1142 type of device, when operated carefully by an experienced operator measures the temperature at which the human eye is capable of detecting the formation of condensed liquid on the cooled mirror. The amount of condensed liquid estimated by Cowper (6) is 76 mg/Nm3 or 0.6 gal/MMscf. The amount of condensed liquid estimated by Bergman, et al. (7) from measurements in actual operations is similar, 0.3 to 0.5 gallon per MMcf (roughly 40 to 65 mg/Nm3).

# DISCUSSION OF THE CONDUMAX TYPE OF EQUIPMENT

Michell Instruments is the CONDUMAX and CONDUMAX II manufacturer (<u>www.michell-instruments.com</u>). A scan of an image of the CONDUMAX II cell from the Michell Instruments website is given in Figure 5.



Figure 5. Scan of CONDUMAX II from Michell Instruments website

Whereas the cooled surface of the ASTM D-1142 device is in the vertical position, the cooled surface of the CONDUMAX II (and CONDUMAX) is in the horizontal position. An diode which emits a beam of visible red light is connected to one of the lead wires at the top of the cell. This light is directed to the cooled surface. The cooled surface has an abraded depression, which when dry, due to the surface geometry and position of the photoelectric detector, causes scattering of the beam of visible red light as described in reference (8). The photoelectric detector is connected to the second of the lead wires at the top of the cell. Figure 6 shows a scan of CONDUMAX II individual parts from the Michell Instruments website.

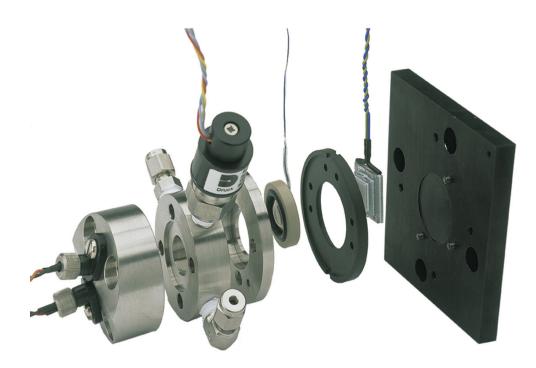


Figure 6. Scan of CONDUMAX II parts, Michell Instruments website

When liquid condenses on the cooled surface, its reflectance increases and the scattered light intensity decreases; this change is detected by the photoelectric detector. In operation, with gas flowing through the cell, the surface is heated to 50 C to establish a dry surface baseline photoelectric detector output. The gas outlet valve is then closed and the surface is cooled while recording the rise above the baseline output of the photoelectric detector. The CONDUMAX II automatically adjusts the cooling rate, starting with a high rate, which is reduced as the dew point is approached. The CONDUMAX II factory setting for the photoelectric signal change is 275 millivolts (mV), which yields a recorded temperature in good agreement with ASTM D-1142 HCDP measurements for gases which have undergone hydrocarbon processing.

Gasunie Engineering and Technology has developed the Gasunie Automatic Condensate Meter (GACOM), which can accurately measure liquid condensed from pipeline natural gas in amounts as small as 5 mg/Nm3 (milligrams per normal cubic meter at 0 C and 1 atmosphere pressure). Panneman (8) has set up the GACOM (Gasunie Automatic Condensate Meter) and the CONDUMAX II with both connected to the same natural gas pipeline sample line in order to compare their data. Panneman measured the amount of liquid condensed in the GACOM equipment at the same temperature at which the CONDUMAX II photoelectric cell was tripped using factory settings (275 millivolts). For four different natural gases at pressures near 400 psia, the GACOM equipment measured between 5 mg/Nm3 and 40 mg/Nm3 (0.04 to 0.3 gal/MMcf).

Panneman (8) has proposed the use of the GACOM equipment for calibration of the CONDUMAX II. In fact, because the GACOM method quantitatively measures the amount of condensed liquid, it can be expected to replace ASTM D-1142, which measures the operational dew point, as the de-facto reference worldwide. The GACOM method would be recommended in the present project if the GACOM equipment were available in Colombia. Because the GACOM equipment is not available in Colombia, it is recommended that the CONDUMAX (or CONDUMAX II) be calibrated using the ASTM D-1142 method, which is presently the de-facto reference.

# **ISOBARIC CONDENSATION FOR GAS COMPOSITIONS USED**

Information on the condensation behavior of a gas near the dew point is valuable for understanding dew point equipment operation. To study the constant pressure (isobaric) condensation behavior of the three gases in Table 1 near the dew point, the Peng-Robinson equation of state (PR EOS) was used to perform flash calculations at a series of temperatures at each of the three pressures, 415 psia, 615 psia and 1025 psia. Figures 7, 8 AND 9 show the results of these calculations for the Cusiana gas, the Ballena-Barranquilla-Cartagena (BBC) gas and the Ballena-Barrancabermeja (BB) gas compositions.

The plots in Figures 7-9 are of PHLC versus temperature in Fahrenheit (F). PHLC is Potential Hydrocarbon Liquid in mg/Nm3 (milligrams of liquid condensed per normal cubic meter at 0 C and 1 atmosphere pressure). The condition PHLC=0.0 is the PR EOS HCDP condition (estimated by the PR EOS).

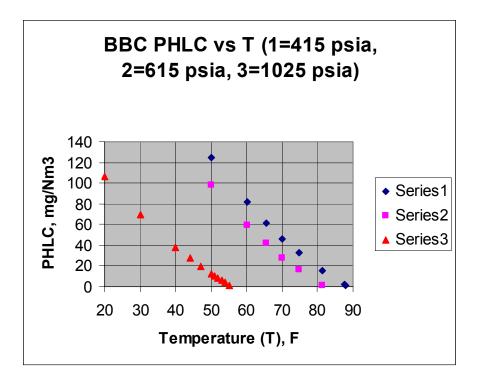


Figure 7. Calculated PHLC versus T for BBC Gas (Table 1)

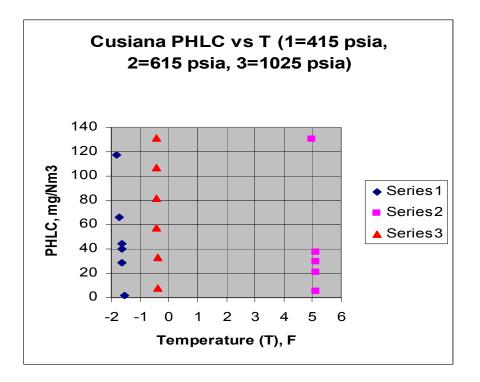


Figure 8. Calculated PHLC versus T for Cusiana Gas (Table 1)

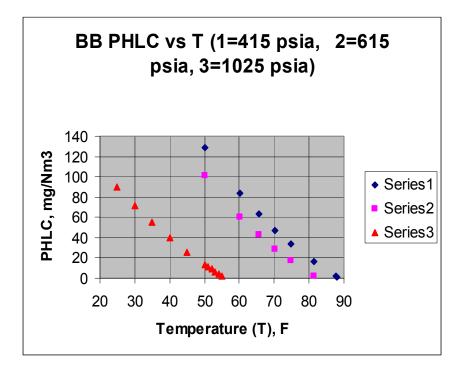


Figure 9. Calculated PHLC versus T for BB Gas (Table 1)

Comparing Figures 7-9, it can be noted that as the temperature of the Cusiana gas is lowered, PHLC=40.0 mg/Nm3 is achieved within 1 F of the PR EOS HCDP whereas the BBC and BB gas temperatures must be lowered more than 15 F below the PR EOS HCDP to reach PHLC=40.0 mg/Nm3. Because of this behavior, the recorded temperature of detection of liquid by either the ASTM D-1142 method or the CONDUMAX (or CONDUMAX II) method will be much closer to the "true" HCDP in the case of the Cusiana gas composition than in the cases of the Ballena-Barranquilla-Cartagena (BBC) gas or the Ballena-Barrancabermeja (BB) gas compositions in Table 1.

A general conclusion which follows from the above discussion of Figures 2-4 is that measurement of the HCDP of a natural gas which has undergone hydrocarbon processing is easier and more accurate than for an unprocessed gas which has a hydrocarbon "tail" extending beyond C10.

# **ISOTHERMAL CONDENSATION FOR COMPOSITIONS USED**

Information on the isothermal (constant temperature) condensation behavior of a gas near the dew point is valuable for understanding constant composition expansion (CCE) dew point equipment operation. To study the isothermal condensation behavior of the three gases in Table 1 near the dew point, the Peng-Robinson equation of state (PR EOS) was used to perform flash calculations at a series of pressures at the PR EOS HCDP temperatures at each of the three pressures, 415 psia, 615 psia and 1025 psia. Figure 10 shows the calculated liquid volume percent for the Cusiana gas at -0.39 F.

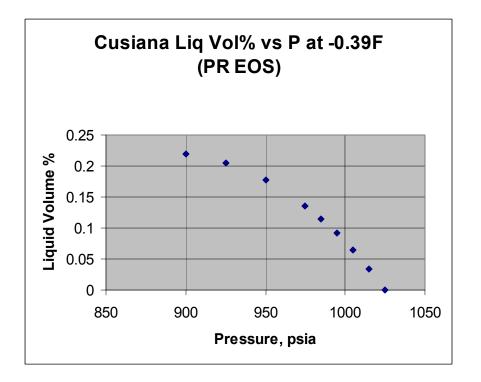


Figure 10. Calculated Liquid Volume %, Cusiana Gas (Table 1)

It can be noted in Figure 10 that the Cusiana gas liquid drop out curve can be extrapolated very easily to the dew point pressure, 1025 psia. Using the Sloane type of constant composition expansion equipment, the initial detection of liquid could be as close to the dew point pressure at 10 psi, where the PR EOS calculated liquid volume percent 0.034% should be visibly detectable. Even if liquid was not detected at this pressure, the next increment at 1005 psia would have

0.064% liquid, which would be easily detectable with a 600 cubic centimeter gas volume in the cell.

From the discussion above, it is clear that the constant composition expansion method could be used for measurements of Cusiana gas dew points at high pressures, so long as temperatures are well below the cricondentherm temperature. However, the constant composition method cannot be used near the cricondentherm temperature or for lower dew point pressures.

Figure 11 shows the calculated liquid volume percent for the Ballena-Barranquilla-Cartagena (BBC) gas at 55.0 F.

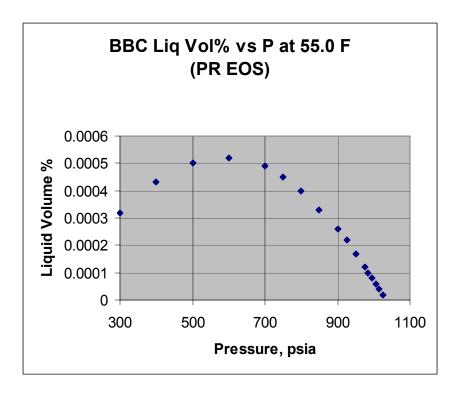


Figure 11. Calculated Liquid Volume %, BBC Gas (Table 1)

It can be noted in Figure 11 that for the Ballena-Barranquilla-Cartagena (BBC) gas, very little condensation of liquid occurs in the constant composition expansion at 55.0 F. The maximum liquid volume percent in Figure 11 is 0.00052%. For a 600 cubic centimeter gas volume in the cell, this would be only 0.003 cubic centimeters of liquid, which, even if detected visually, could not be measured quantitatively. The behavior of the Ballena-Barrancabermeja (BB) gas would be similar to the behavior shown in Figure 11 for the Ballena-Barranquilla-Cartagena (BBC) gas because of the similarities in the compositions of these gases. As a consequence of this behavior, it would not be practical to use the constant composition expansion method for measurements of the dew points of the Barranquilla-Cartagena (BBC) gas or the Ballena-Barrancabermeja (BB) gas.

From the discussion above, it is concluded that the constant composition expansion method is not practical for dew point measurements for the Colombian natural gases considered in this project, and so the method is not recommended.

#### **UNCERTAINTY ESTIMATION**

For natural gases which have undergone hydrocarbon processing, there are literature references which can be used as the basis for uncertainty estimates for HCDP measurements. For unprocessed natural gases which have hydrocarbon "tails" extending beyond C10, very little HCDP measurement uncertainty information is available. Conversations with individuals who have had varied experience with hydrocarbon dew point measurements indicate that the measurement uncertainty increases as the molecular weights of the trace components increase; however, these conversations did not supply quantitative uncertainty information.

The information which has been presented in this report demonstrates that the ASTM D-1142 method measures the operational dew point and that the quantity of liquid which would be condensed from the gas at the operational dew point is roughly 40 mg/Nm3 or 0.3 gal/MMscf. Therefore, the uncertainty estimates presented here are in relation to the operational dew point. The operational dew point will be defined here as the average of a series of ASTM D-1142 HCDP measurements on the same gas at the same pressure, such that an additional measurement does not change the average value significantly. It will be noted later that the standard deviation of such repeat measurements (that is, the precision) is expected to be roughly 2.4 F.

## ASTM D-1142 UNCERTAINTY ESTIMATION

According to Warner, et al. (9), repeat measurements by eight different individuals indicated that for seven mixtures studied, the ASTM D-1142 hydrocarbon dew point temperature measurement standard deviation about the mean was 2.4 F. Five of these mixtures were certified, synthetically prepared mixtures which contained no hydrocarbons with molecular weights greater that decane. These measurements were made in the laboratory; field measurements would be expected to have greater uncertainty than 2.4 F.

Dustman, Drenker, Bergman, and Bullin (10) have presented a large amount of information regarding the ASTM D-1142 method for natural gas hydrocarbon dew point measurement. Three points made in Dustman, et al. (10) are of interest to the present study. First, Dustman, et al. demonstrate that both the Peng-Robinson (PR) and the Soave-Redlich-Kwong (SRK) equations of state (EOS) yield calculated HCDP values within +/- 3 F of ASTM D-1142 measurements made in the laboratory by Warner et al. (9) with five simulated natural gases prepared gravimetrically with n-decane as the highest molecular weight component. Figure 12 shows these results (two points at the highest temperature superimpose).

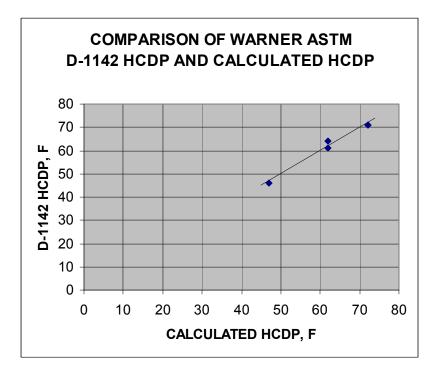


Figure 12. ASTM D-1142 HCDP versus SRK Calculated HCDP for Mixtures Prepared Gravimetrically

Second, Dustman, et al. demonstrate that ASTM D-1142 measurements in the field at Questar Pipeline Company sites by two technicians agree with SRK EOS calculations with an average absolute deviation of 5.2 F when the API 14.1 purge-and-fill sampling method (11) and GPA 2286 extended analysis method (12) were used. Figure 13 shows these results. The deviation for a point would be expected to be due to the uncertainty in the extended chromatographic analysis, the uncertainty in the SRK EOS and the uncertainty in the ASTM D-1142 field measurement by the technician. Therefore, these ASTM D-1142 measurements tend to support the conclusion that careful work by a technician has a precision near the precision reported by Warner, et al., that is, 2.4 F.

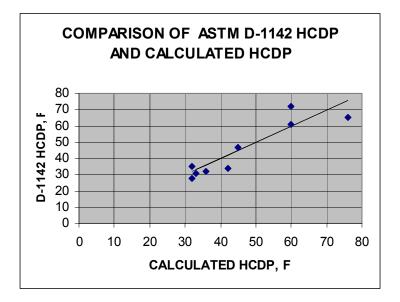


Figure 13. ASTM D-1142 HCDP versus Extended Analysis SRK Calculated HCDP for Field Measurements by Two Technicians

Third, Dustman, et al. demonstrate that ASTM D-1142 measurements in the field at Questar Pipeline Company sites by one technician who was hurried because of an overload of tasks, agree with SRK EOS calculations with an average absolute deviation of 17.8 F when the API 14.1 purge-and-fill sampling method (11) and GPA 2286 extended analysis method (12) were used. Figure 14 shows these results.

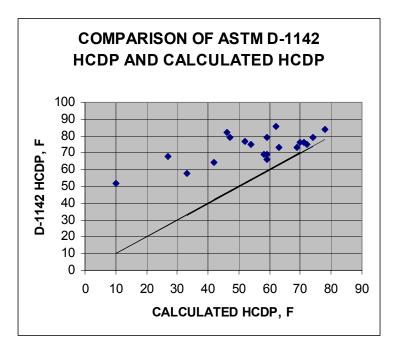


Figure 14. ASTM D-1142 HCDP versus Extended Analysis SRK Calculated HCDP for Field Measurements by Hurried Technician

To summarize, Dustman, et al. demonstrate that both the Peng-Robinson (PR) and the Soave-Redlich-Kwong (SRK) equations of state (EOS) yield calculated HCDP values within +/- 3 F of ASTM D-1142 measurements made in the laboratory by Warner et al. (3) with five simulated natural gases prepared gravimetrically with n-decane as the highest molecular weight component. In the field, the API 14.1 purge-and-fill sampling method was used at Questar Pipeline Company sites to obtain samples which were analyzed using the GPA 2286 extended analyses. ASTM D-1142 HCDP field measurements by two technicians agree with extended analysis SRK calculated HCDP values with an average absolute deviation of 5.2 F. Twenty ASTM D-1142 HCDP field measurements by a hurried technician were all greater than extended analysis SRK calculated HCDP values and had an average absolute deviation of 17.8 F.

#### CONDUMAX UNCERTAINTY ESTIMATION

In a discussion of the CONDUMAX II analyzer, Benton (13) states, "a factory default trip value of 275 millivolts has been proven to provide comparative measurements to those obtained by an experienced operator applying the manual, visual technique."

Benton (13) points out that the CONDUMAX II can be used to run a sensitivity calibration curve for the natural gas being analyzed. CONDUMAX sensitivity calibration data at 415 psia for the Ballena-Barranquilla-Cartagena (BBC) gas have been made available for the present project by Mr. Alejandro Villalba of Promigas (14). It has been very useful to this project to use the CONDUMAX sensitivity calibration data provided by Mr. Villalba. Shown in Figure 15 are CONDUMAX sensitivity calibration data for three separate days of operation of the Ballena-Barranquilla-Cartagena (BBC) gas pipeline.

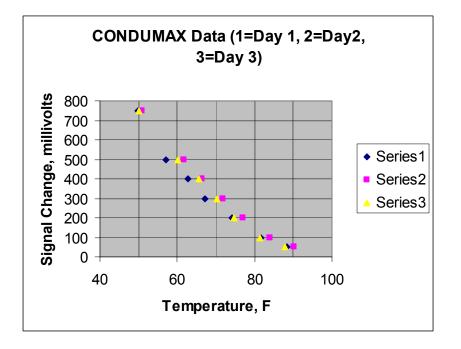


Figure 15. CONDUMAX sensitivity calibration data for BBC gas

The similarity of the Figure 16 plot of PR EOS calculated PHLC versus temperature at 415 psia for the BBC gas composition in Table 1 and the curves in Figure 15 can be noted.

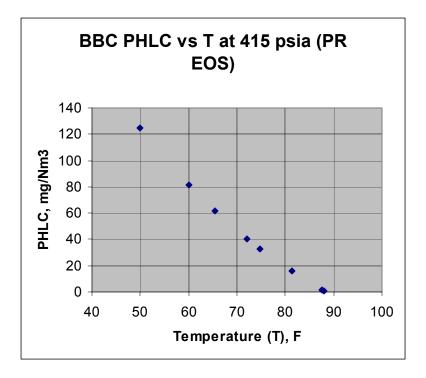


Figure 16. PR EOS Calculated PHLC for BBC Gas (Table 1)

The C11+ mole percent in the BBC gas composition in Table 1 was chosen to yield a calculated PHLC of 40 mg/Nm3 at approximately the temperature at which the CONDUMAX signal change was 275 millivolts for the day 3 CONDUMAX data in Figure 15, 72.0 F. For the BBC gas composition in Table 1, the dew point calculated at 415 psia with the Peng-Robinson equation of state (PR EOS) is 88.0 F. Thus, there is a 16 F difference between the PR EOS HCDP of 88.0 F and the CONDUMAX operational HCDP of 72.0 F (the CONDUMAX 275 millivolt condition) for the BBC gas composition in Table 1.

The answer to a central question remains uncertain. That question is whether the CONDUMAX 275 millivolt condition corresponds to a point inside the two phase region where the natural gas has dropped out a fixed amount of liquid (for example, 40 mg/Nm3). The information available to the Consultant Dr. Kenneth E. Starling, some of which is propriety, suggests a typical value of 40 mg/Nm3. Unfortunately, the amount of data available is insufficient to establish whether the amount of liquid is a constant and if it is a constant, the numerical quantity of liquid. The following literature references suggest about 40 mg/Nm3 would be condensed to the temperature of the 275 millivolt CONDUMAX II factory setting.

1. For the ASTM D-1142 type of device, when operated carefully by an experienced operator, the amount of condensed liquid estimated by Cowper (6) is 76 mg/Nm3 or 0.6 gal/MMscf. The amount of condensed liquid estimated by Bergman, et al. (7) from measurements in actual operations is similar, 0.3 to 0.5 gallon per MMcf (roughly 40 to 65 mg/Nm3).

2. Benton (13) indicated that the CONDUMAX II factory setting of 275 millivolts yields a recorded temperature in good agreement with ASTM D-1142 HCDP measurements.

3. Panneman (8) measured the amount of liquid condensed in the GACOM equipment at the same temperature at which the CONDUMAX II photoelectric cell was tripped using factory settings (275 millivolts). For four different natural gases at pressures near 400 psia, the GACOM equipment measured between 5 mg/Nm3 and 40 mg/Nm3 (0.04 to 0.3 gal/MMcf).

Figure 17 is a scan of a figure presented by Panneman (8), which shows CONDUMAX II sensitivity calibration curves for three natural gases. The three gases, from left to right on Figure 17, are the H-gas (2), the H-gas (1) and the L-gas. Comparing the BBC gas CONDUMAX sensitivity curves in Figure 15 to the curves in Figure 17, it can be noted that the BBC curves are most similar to the L-gas curve. Panneman (8) presents detailed information for the L-gas which shows that the temperature of the CONDUMAX II 275 millivolt factory setting corresponds to a simultaneous GACOM measurement of PHLC=40 mg/Nm3.

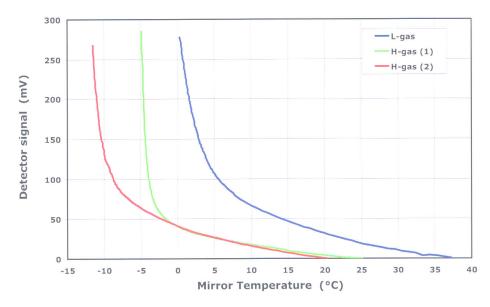


Figure 17. Scan of figure from Panneman, reference (8)

Note in Figure 17 the steep rise of the CONDUMAX II detector signal for the H-gas (1) as temperature is decreased. Also, note in Figure 8 the steep rise of calculated PHLC at 415 psia for the Cusiana gas composition in Table 1. The similarities of these curves suggest that a measured CONDUMAX II sensitivity calibration curve for the Cusiana gas might have the general shape of the H-gas (1) curve in Figure 17. If this were the case, then the use of the CONDUMAX II factory setting of 275 millivolts, even if not corresponding to PHLC= 40 mg/Nm3, would still record a temperature within 1.0 F of the 40 mg/Nm3 value.

In summary, even if PHLC=40 mg/Nm3 at 275 millivolts CONDUMAX II detector signal is not a fixed constant for all natural gases, it probably is a reasonable value for the BBC and BB gases. Further, for the Cusiana gas, the use of the CONDUMAX factory setting of 275 millivolts probably yields a recorded temperature within 1.0 F of the temperature at PHLC=40 mg/Nm3.

#### **CALIBRATION OF CONDUMAX ANALYZERS WITH ASTM D-1142**

Arguments presented in this report indicate that the recorded temperature for the CONDUMAX (or CONDUMAX II) with the detector signal factory setting of 275 millivolts probably corresponds closely to the ASTM D-1142 operational dew point. However, the only way to be assured measurements with the two methods agree is to calibrate the CONDUMAX (or CONDUMAX II) using the ASTM D-1142 method.

Although it is beyond the scope of this project to discuss calibrations in detail, a few comments and suggestions are given here. First, for most gases and conditions, the CONDUMAX type of device is much more precise than the ASTM D-1142 device. Consequently, ASTM D-1142 calibration measurements should be made by a competent and experienced technician. When a significant change in the detector setting will result from the calibration, a competent and experienced supervisor should personally repeat the technician's calibration for verification.

When the change in the detector setting will result from the calibration is to a value below about 175 millivolts, verification checks should be performed for both the CONDUMAX (or CONDUMAX II) and the ASTM D-1142 methods. The CONDUMAX (or CONDUMAX II) has decreased precision as the detector signal is decreased (for example, the precision might be 0.1 F at 275 mV, 1.0 F at 175 mV and 10.0 F at 75 mV). Several repeats of the CONDUMAX (or CONDUMAX II) calibration sensitivity curves can disclose the CONDUMAX (or CONDUMAX II) precision. This procedure will yield a plot somewhat like that for the BBC gas in Figure 15, where the three different temperatures at a given detector signal value is due in part to the instrument precision (and in part to the daily changes in flowing gas composition).

The importance to the CONDUMAX (or CONDUMAX II) calibrations of the ASTM D-1142 measurements should be taken very seriously. Studies should be performed to establish appropriate operating ranges for the ASTM D-1142 method. The natural gas must be maintained in the gas phase between the pipeline and the ASTM D-1142 device.

For a given pipeline gas and pressure, a matrix of the combinations of the range of natural gas rates and range of temperature cooling rates which yield statistically the same operational dew point can be determined. Low gas flow rates will allow equilibrium to be approached more closely than high gas flow rates. High mirror cooling rates can yield erroneous data due to temperature lag; low mirror cooling rates reduce the lag effect and allow greater precision in recording the temperature at which liquid is detected visually.

This above information will yield the mean value and standard deviation of the measurements. This type of information could first be developed in the laboratory and then tested for the degree of reproducibility in the field reproducibility in the field. The laboratory set up could be retained for technician training.

#### CONSULTANT'S UNCERTAINTY ESTIMATES

Table 2 shows uncertainty estimates for the three hydrocarbon dew point measurement methods for the three compositions in Table 1 at the three pressures, 415, 615 and 1025 psia. The designation N/A is shown for conditions and gas compositions where it is believed the constant composition expansion method can not be utilized.

		Estimated Constant Composition Expansion	Estimated ASTM D-1142	Estimated Condumax	Estimated Condumax Calibration	Estimated Condumax Overall
	Pressure,	Uncertainty	Uncertainty	Repeatibility	Uncertainty	Uncertainty
GAS	psia	Degrees F	Degrees F	Degrees F	Degrees F	Degrees F
Cusiana	415.0	N/A	2.4	1.5	2.4	2.8
Cusiana	615.0	N/A	2.4	1.5	2.4	2.8
Cusiana	1025.0	2.4	2.4	1.5	2.4	2.8
BBC	415.0	N/A	2.4	3.0	2.4	3.8
BBC	615.0	N/A	2.4	3.0	2.4	3.8
BBC	1025.0	N/A	2.4	3.0	2.4	3.8
BB	415.0	N/A	2.4	3.0	2.4	3.8
BB	615.0	N/A	2.4	3.0	2.4	3.8
BB	1025.0	N/A	2.4	3.0	2.4	3.8

Table 2. Uncertainty Estimates (relative to ASTM D-1142 mean)

The uncertainty estimates in Table 2 are relative to ASTM D-1142 mean, that is, the operational dew point. Therefore, the uncertainty estimates presented here are in relation to the operational dew point. The operational dew point is defined here as the average (or mean) of a series of ASTM D-1142 HCDP measurements on the same gas at the same pressure, such that an additional measurement does not change the average value significantly. It was noted earlier that the

standard deviation of such repeat measurements (that is, the precision) is expected to be roughly 2.4 F.

The CONDUMAX uncertainty is considered to be attributable to the CONDUMAX repeatability and the uncertainty of the calibration by the ASTM D-1142 method. The estimates for the CONDUMAX repeatability are based for CONDUMAX sensitivity calibration data for different gases. For gases such as the Cusiana gas, which have steep PHLC versus temperature curves, the CONDUMAX repeatability is better than for gases with long hydrocarbon tails, such as the BBC gas and the BB gas. The sum of the squares of the CONDUMAX repeatability and the calibration uncertainty by the ASTM D-1142 method is the square of the overall CONDUMAX uncertainty.

# CONCLUSIONS

- 1. The ASTM D-1142 method is the de-facto reference worldwide.
- 2. Although the ASTM D-1142 does not measure the true dew point, it measures the operational dew point.
- 3. The liquid condensed in a careful ASTM D-1142 HCDP measurement is considered to be roughly 40 to 76 mg/Nm3.
- 4. The fact that the CONDUMAX II factory setting of 275 millivolts corresponds to the ASTM D-1142 measurement indicates that the CONDUMAX II measures the operational dew point.
- 5. The fact that the GACOM equipment indicated 5 to 40 mg/Nm3 at temperatures where the CONDUMAX II factory setting of 275 millivolts occurred, indicates that no more liquid than approximately 40 mg/Nm3 is present for either a CONDUMAX II or an ASTM D-1142 operational dew point measurement.
- 6. Calibration of the CONDUMAX (or CONDUMAX II) using the ASTM D-1142 method will insure that it is measuring the operational dew point.

### RECOMMENDATIONS

1. It is recommended that CREG decide upon a Reference Hydrocarbon Dew Point Measurement Method to be used in Colombia.

2. It is recommended that CREG require in Colombia that the Reference Hydrocarbon Dew Point Measurement Method be used for the calibration of other hydrocarbon dew point measurement equipment.

3. It is recommended that CREG require in Colombia that measurements using the Reference Hydrocarbon Dew Point Measurement Method be utilized in resolutions of disputes between parties involving hydrocarbon dew points.

4. It is recommended that CREG regularly review technology availability for potential improvement or replacement of the Reference Hydrocarbon Dew Point Measurement Method (for example, the highly accurate Gasunie Engineering and Technology GACOM method, which is not yet commercially available in Colombia).

5. It is believed by the Consultant Dr. Kenneth E. Starling that, as of November 2006, the most appropriate choice for the Reference Hydrocarbon Dew Point Measurement Method in Colombia is the ASTM D-1142 method (the ASTM D-1142 method, which does not require calibration, has been a worldwide de-facto reference in the past).

6. It is believed by the Consultant Dr. Kenneth E. Starling that the use of online hydrocarbon dew point analyzers is pragmatic for efficient and economic gas quality control. Consideration of only one type of online analyzer was specified for the present study, the CONDUMAX/CONDUMAX II type, which Gasunie Engineering and Technology has proven can be adjusted to closely reproduce a calibration measurement. Ongoing and future studies will provide additional evaluations of online analyzers.

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# **APPENDIX 1**

# PROPOSAL FOR CONTRACTING OF EXPERT CONSULTANT DR. KENNETH E. STARLING FOR HYDROCARBON DEW POINT DETERMINATION

## BACKGROUND

This proposal was prepared by Dr. Kenneth E. Starling, PhD, an expert consultant in the area of Natural Gas Quality. A resume for Dr. Starling is supplied separately. On November 4, 2005, Dr. Starling was contacted by Mr. Alejandro Villalba of Promigas. Mr. Villalba stated that the Colombian natural gas hydrocarbon dew point (HCDP) contracting parties desired that I prepare a proposal as an expert consultant with the objective discussed below.

## OBJECTIVE

To evaluate the following three (3) methods for determining the natural gas hydrocarbon dew point in transportation systems:

- 1. CONDUMAX hydrocarbon dew point on line analyzer;
- Experimental CCE (constant composition expansion) test, based on API RP 44;
- Manual determination through the cooled mirror methodology (flat), as per standard ASTM D 1142-95, with a tolerance of more or less 1°C;

and to recommend the best of the three methods for measurement thereof at the Points of Entry of the National Transport System in Colombia, under performance and operability criteria.

## **OBJECTIVE (Expert Consultant's Comments)**

Methods for determining the natural gas hydrocarbon dew point in transportation systems have been carefully studied by Gasunie Research in the Netherlands for more that 20 years. The Expert Consultant Dr. Kenneth E. Starling consulted with Gasunie in 1985 regarding the planning of a major project carried out in the period 1985-1993. This project involved the development of an extensive vapor-liquid equilibrium data base, the development of a highly

accurate extended natural gas composition determination method and development of a highly accurate equation of state for liquid condensation from natural gases. This was excellent work but the industry found it difficult to implement, so in the 1990s the ISO 6570 manual gravimetric method for measuring liquid condensed near the dew point was developed by Gasunie. Subsequently, Gasunie developed GACOM (Gasunie Automatic Condensate Meter) for online measurement of liquid condensed from a natural gas pipeline stream. GACOM cools the natural gas to any specified (set point) temperature and determines the liquid condensed.

Experimental data indicate that devices based on the Bureau of Mines chilled mirror method tend to indicate dew points lower than temperatures where liquid is detected using GACOM. Very recently, Michell Instruments Ltd. developed the Condumax II hydrocarbon dew point online analyzer. Gasunie, in collaboration with Michell Instruments, has reported that GACOM can be used to calibrate the Condumax II for hydrocarbon dew point measurement within 0.5 C (0.9 F).

Based on the work reported by Gasunie and conversations of Expert Consultant Dr. Kenneth E. Starling with Mr. Henk Jan Panneman of Gasunie and Mr. Arthur Scheffer of Michell Instruments, it is probable that if GACOM were available for purchase, GACOM could be used to evaluate quantitatively each of the three (3) methods for determining the natural gas hydrocarbon dew point in transportation systems stated in the WORK SCOPE. It would then be possible to recommend the best of the three methods for measurement of natural gas hydrocarbon dew points at the Points of Entry of the National Transport System in Colombia, under performance and operability criteria. It is probable that GACOM could then be used for routine calibrations of the equipment used in the recommended method.

Unfortunately, when I contacted Gasunie in May, 2005, the GACOM equipment was not commercially available for purchase. Therefore, the use of GACOM in Colombia must wait until GACOM is commercially available for purchase. Nevertheless, I believe that I am in the best position possible to evaluate which of the three methods is the best for measurement of natural gas hydrocarbon dew points at the Points of Entry of the National Transport System in Colombia, under performance and operability criteria.

## SCOPE

Perform a technical evaluation the following three (3) methods for determining the natural gas hydrocarbon dew point in transportation systems:

CONDUMAX hydrocarbon dew point on line analyzer; Experimental CCE (constant composition expansion) test; Manual determination through the cooled mirror methodology (flat), as per standard ASTM D 1142-95.

Recommend the best of the three methods for measurement thereof at the Points of Entry of the National Transport System in Colombia, under performance and operability criteria.

# SCOPE (Expert Consultant's Comments)

It is proposed that the Expert Consultant Dr. Kenneth E. Starling perform a technical evaluation to estimate the uncertainty of each method for a range of natural gas compositions and pipeline operating pressures of interest to the contracting parties.

Three natural gas compositions and three pipeline operating pressures are to be provided to the Expert Consultant Dr. Kenneth E. Starling to perform a technical evaluation to estimate the uncertainty of each method at each condition. This evaluation exercise involves 27 uncertainty estimations (3 methods times 3 compositions times 3 pressures).

I wish to evaluate the CONDUMAX II, not earlier versions. I believe that the CONDUMAX II has received a valid test by Gasunie. This opinion is based on my meeting with Mr. Henk Jan Panneman of Gasunie and Mr. Arthur Scheffer of Michell Instruments, the CONDUMAX II manufacturer, in regard to the Gasunie evaluation of CONDUMAX II using the Gasunie Automatic Condensation Meter, GACOM. For the constant composition expansion test, I wish to evaluate the ACB constant composition expansion equipment and test method, because I have previously studied this method in detail with the cooperation of Core Laboratories and information from the equipment manufacturer. The ACB equipment, manufactured in France, was designed specifically for constant composition expansion tests and therefore I believe it is a good choice for evaluation of the constant composition expansion method.

The manual determination through the cooled mirror methodology (flat), as per standard ASTM D 1142-95 (Bureau of Mines dewscope) is the traditional method for measuring natural gas dew points. I have done a lot of unpublished work in analyzing how the Bureau of Mines dewscope operates and why different uncertainties result for different gas compositions and different pressures.

I believe that the objectives of this project can be achieved with this scope of work.

## DELIVERABLES

Recommend an industry accepted international methodology to determine the hydrocarbon dew point at the Point of Entry of the National Transport System. This recommendation will be supported by a written report and an executive presentation to the contracting parties. This written report is referred to herein as the final report.

Deliver as part of the final report an interpretation of the recommended methodology's technical basis, according to standards and practices recognized internationally.

Deliver as part of the final report critical aspects found and recommendations for avoiding problems.

### **DELIVERABLES (Expert Consultant's Comments)**

The description of the deliverables requires one report and one presentation. This is acceptable to the Expert Consultant Dr. Kenneth E. Starling.

## **QUALIFICATIONS (Expert Consultant's Comments)**

The Expert Consultant Dr. Kenneth E. Starling has been a member of the AGA Transmission Measurement Committee since 1980. Dr. Kenneth E. Starling was the author of AGA Report No. 8 (1985) and co-author of AGA Report No. 8 (1992, 1994).

The Expert Consultant Dr. Kenneth E. Starling has served on the API Manual of Petroleum Measurement Standards Chapter 14 Section 1 Working Group since 2001. He was a consultant to the dew point project in 2001.

The Expert Consultant Dr. Kenneth E. Starling performed vaporliquid equilibrium measurements while employed by the Institute of Gas Technology and has witnessed dew point measurements as a consultant.

The Expert Consultant Dr. Kenneth E. Starling participated in the development of natural gas vapor-liquid equilibrium and viscosity measurement equipment while employed by the Institute of Gas Technology.

The Expert Consultant Dr. Kenneth E. Starling has managed numerous research projects as a professor at the University of Oklahoma from 1966 through 1995.

The Expert Consultant Dr. Kenneth E. Starling has published more than 100 technical articles, principally in the areas of thermophysical properties and natural gas measurement.

The Expert Consultant Dr. Kenneth E. Starling was Chairman of the Executive Committee of the International School of Hydrocarbon Measurement from 1982 through 1990.

### **EXECUTION SITE (Expert Consultant's Comments)**

The work performed in this project by the Expert Consultant Dr. Kenneth E. Starling will be carried out in the United States of America except for a trip to Bogota, Colombia for an executive presentation to the contracting parties.

## **EXECUTION TIME (Expert Consultant's Comments)**

The Expert Consultant Dr. Kenneth E. Starling would like to start the work the first week in January, 2006, complete the final report within four weeks time and make the executive presentation to the contracting parties in Bogota by the middle of February, 2006.

The Expert Consultant Dr. Kenneth E. Starling will use his best efforts to complete the aforementioned deliverables within the above time period.

### **CONTRACT COST (Expert Consultant's Comments)**

The Expert Consultant Dr. Kenneth E. Starling will perform the work discussed above for a fee of \$38,000.00 (United States Dollars). Estimated travel cost in the amount of \$2,000.00 for one trip from Norman, Oklahoma USA to Bogota, Colombia for an executive presentation to the contracting parties is included in the above fee.

If additional work or additional travel is desired by the contracting parties, this additional work or additional travel must be paid for separately.

# **APPENDIX 2**

## REQUEST FOR SAMPLING, ANALYSIS INFORMATION FROM CONSULTANT DR. KENNETH E. STARLING

#### BACKGROUND

This request was prepared by Dr. Kenneth E. Starling, consultant in the area of Natural Gas Quality. On January 23, 2006 Dr. Starling had a telephone conference meeting with Mr. Jorge Duran of CREG and Mr. Alejandro Villalba of Promigas. Mr. Duran and Mr. Villalba stated that the Colombian natural gas hydrocarbon dew point (HCDP) contracting parties desired that I prepare a statement of the information that I would like to have regarding sampling and analysis for the three natural gases to be sampled.

#### SAMPLING

I would like to know the pipeline location where the sample is obtained, the date and time the sample was obtained, the sampling method, the flowing temperature and the flowing pressure in the pipeline when the sample was obtained. If the sample is obtained using an industry standard method, such as one of the methods in API MPMS Chapter 14.1 or GPA 2166 I would like to know the method used. If an industry standard method is not used, I would like to have a brief description of the method used.

#### HANDLING AND CHROMATOGRAPHIC ANALYSIS

The natural gas in the sample cylinder should be maintained as a well mixed single phase gas mixture before charging to the gas chromatograph. Mixing can be aided by a nonuniform heat source. such as putting a lamp at the base of a vertical cylinder. Maintaining the mixture as single phase is aided by raising the temperature above the flowing gas temperature; 40 F is usually sufficient. I would like to know the chromatographic method used to analyze the gas I would prefer an extended analysis method, for composition. example GPA 2286. I recommend that gas from the same cylinder be analyzed at two separate laboratories. For each component, the difference in the mole percentages from the two laboratories will be an estimate of the component mole percent uncertainty. The maximum number of significant figures in the mole percentages of each component from the chromatographic analyses should be reported.

# **APPENDIX 3**

# RECOMMENDED GAS COMPOSITIONS AND PRESSURES FOR HCDP UNCERTAINTY ESTIMATES By Dr. Kenneth E. Starling

## BACKGROUND

The following is a portion of the proposal to CREG by Dr. Kenneth E. Starling, consultant in the area of Natural Gas Quality.

## SCOPE

Perform a technical evaluation the following three (3) methods for determining the natural gas hydrocarbon dew point in transportation systems:

CONDUMAX hydrocarbon dew point on line analyzer; Experimental CCE (constant composition expansion) test; Manual determination through the cooled mirror methodology (flat), as per standard ASTM D 1142-95.

Recommend the best of the three methods for measurement thereof at the Points of Entry of the National Transport System in Colombia, under performance and operability criteria.

## SCOPE (Expert Consultant's Comments)

It is proposed that the Expert Consultant Dr. Kenneth E. Starling perform a technical evaluation to estimate the uncertainty of each method for a range of natural gas compositions and pipeline operating pressures of interest to the contracting parties.

Three natural gas compositions and three pipeline operating pressures are to be provided to the Expert Consultant Dr. Kenneth E. Starling to perform a technical evaluation to estimate the uncertainty of each method at each condition. This evaluation exercise involves 27 uncertainty estimations (3 methods times 3 compositions times 3 pressures).

## **RECOMMENDED GAS COMPOSITIONS**

Chromatographic analyses from three laboratories for each of three natural gas pipeline mixtures have been provided by CREG to Dr. Starling. There is generally good agreement between laboratories for nitrogen, carbon dioxide and the hydrocarbons with 1 to 5 carbon atoms. The agreement between laboratories for hydrocarbons with 6 or more carbon atoms (hexanes plus or C6+) is generally not good.

Because the C6+ hydrocarbons have large influences on the HCDP (hydrocarbon dew point) and the amount of liquid condensed near the HCDP, additional information must be introduced to insure that the compositions used in the project yield predicted behavior in close approximation to the behavior experienced in actual field or processing operations.

The Cusiana gas is processed before it undergoes custody transfer and enters the gas transmission pipeline. Because the conditions at the last vapor-liquid separation point are known, these conditions can be used to adjust the mole% (mole percentage) values for the highest carbon number components and perhaps extend the number of components slightly for improved consistency with the known There are smaller differences between the C6+ conditions. component mole percentages reported for the three laboratories for the Cusiana gas than the two Guajira gases. Therefore, it is recommended that the uncertainty estimations be based on using the average component mole percentages reported for the three laboratories for the Cusiana gas, with possible adjustment of the mole% (mole percentage) values for the highest carbon number components and perhaps extension of the number of components for improved consistency with the known separator conditions.

The results of this averaging procedure for the Cuisiana gas (without adjustments for separator conditions) are shown on Figure 1. Figure 1 is a plot of the natural logarithm of the mole fraction (Zi) versus carbon number (Cni). Figure 1 shows the plot for ethane (Cn2=2) through decanes (Cn10=10) for the analyses from Instituto Colombiano del Petroleo (ICP), Core Laboratories Venezuela (CLV)

and Core Laboratories Aberdeen (CLA), along with the values from the average composition from the three laboratories combined.

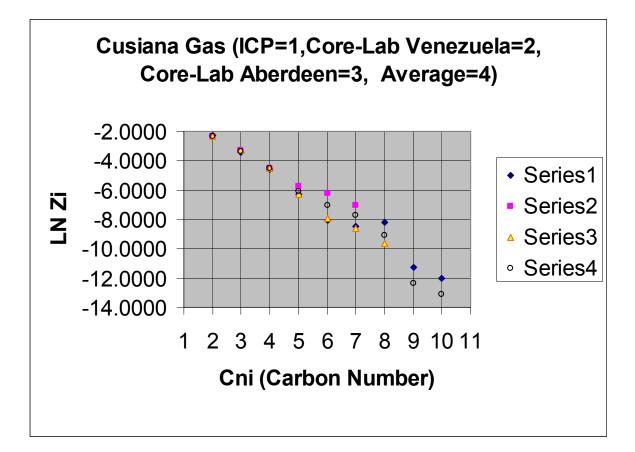


Figure 1. Comparison of Cuisiana Gas Compositions

Because the Guajira gas is produced from a non-associated reservoir and the gas does not undergo hydrocarbon processing, it is not possible to adjust the composition using an operating condition. However, Mr. Alejandro Villalba of Promigas has provided Condumax sensitivity calibration data, along with chromatographic analyses for three separate days of operation of the Ballena-Barranquilla-Cartagena (BBC) gas pipeline. The average C6+ mole% from these three analyses is 0.0167 mole%. It will be very useful to the HCDP project to use the Condumax sensitivity calibration data provided by Mr. Villalba. To be consistent with these Condumax data, the C6+ mole% of the gas should be 0.0167 mole%. Therefore, it is recommended for the HCDP uncertainty estimations for the BBC gas that an adjusted gas composition be determined in the following way. First, the C6+ mole% from the three independent laboratory analyses are adjusted to 0.0167 mole%, while maintaining each C6+ component mole percentage in the reported ratio to the C6+ mole%. The adjusted total mole% for the non C6+ components then is (100.0 – 0.0167) and each non C6+ component mole percentage is maintained in the reported ratio to the non C6+ mole%. The adjusted mole percentages for each component for the three laboratories will then be averaged to obtain the composition used for the HCDP uncertainty estimations. This method insures that the pattern of the C6+ portion of the adjusted BBC gas composition follows the patterns of the C6+ portions from the extended analyses reported by the three laboratories and also corresponds to the C6+ mol% measured at the time of the Condumax data.

The results of this procedure for the Ballena-Barranquilla-Cartagena (BBC) gas are shown in Figure 1.

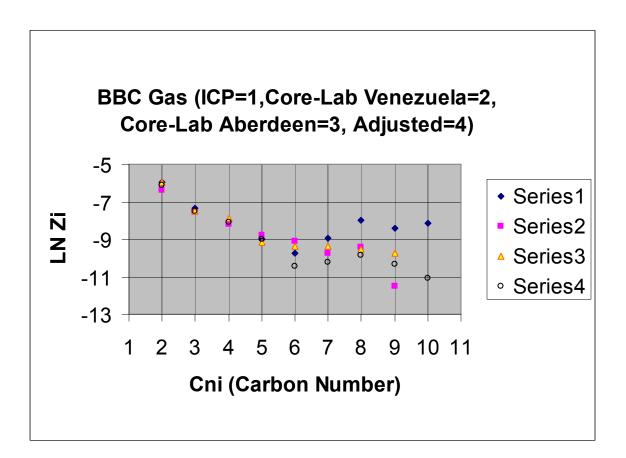
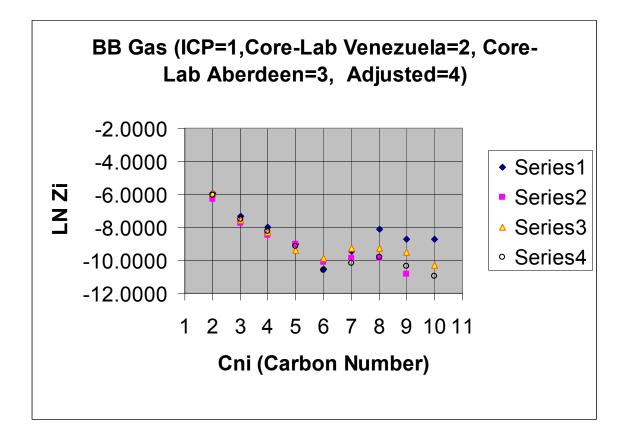


Figure 2. Comparison of Ballena-Barranquilla-Cartagena (BBC) Gas Compositions

Figure 2 is a plot of the natural logarithm of the mole fraction (Zi) versus carbon number (Cni). Figure 2 shows the plot for ethane (Cn2=2) through decanes (Cn10=10) for the analyses from Instituto Colombiano del Petroleo (ICP), Core Laboratories Venezuela (CLV) and Core Laboratories Aberdeen (CLA), along with the values from the adjusted Ballena-Barranquilla-Cartagena (BBC) gas composition from the three laboratories combined.

It is recommended that the same procedure be used to obtain the adjusted composition for the Ballena-Barrancabermeja (BB) gas HCDP estimations. The adjusted C6+ mole% of 0.0167 mole% is recommended unless a more appropriate value is determined.



The results of this procedure for the Ballena-Barrancabermeja (BB) gas are shown in Figure 3.

Figure 3. Comparison of Ballena- Barrancabermeja (BB) Gas Compositions

Figure 3 is a plot of the natural logarithm of the mole fraction (Zi) versus carbon number (Cni). Figure 3 shows the plot for ethane (Cn2=2) through decanes (Cn10=10) for the analyses from Instituto Colombiano del Petroleo (ICP), Core Laboratories Venezuela (CLV) and Core Laboratories Aberdeen (CLA), along with the values from the adjusted Ballena-Barrancabermeja (BB) gas composition from the three laboratories combined.

## **RECOMMENDED PRESSURES**

As noted in the proposal scope, three natural gas compositions and three pipeline operating pressures are to be provided to the Expert Consultant Dr. Kenneth E. Starling to perform a technical evaluation to estimate the uncertainty of each method at each condition.

The following pressures are recommended: 1025 psia, 615 psia and 415 psia. These recommended pressures are based on the objectives discussed below.

First, it is reasonable to make uncertainty estimates at a typical transmission pipeline operating pressure. The pressure of 1025 psia is near the pipeline pressures at the sample points for both the Ballena-Barranquilla-Cartagena (BBC) gas sample and the Ballena-Barrancabermeja (BB) gas sample. The pipeline pressure at the sample point for the Cusiana gas sample is 1212 psia, which is too close to the cricondenbar pressure for this gas (above the cricondenbar pressure, the gas remains one phase at all temperatures of practical interest).

Second, it is reasonable to make uncertainty estimates at pressures near the pressure where the maximum dew point temperature is expected to occur (the cricondentherm temperature). For both the Ballena-Barranquilla-Cartagena (BBC) gas sample and the Ballena-Barrancabermeja (BB) gas sample, the cricondentherm pressure is expected to be near 415 psia. For the Cuisiana gas sample, the cricondentherm pressure is expected to be near 615 psia. Further justification for the recommendation of the pressure of 415 psia is provided by the fact that the Condumax sensitivity calibration data for the Ballena-Barranquilla-Cartagena (BBC) gas provided by Mr. Alejandro Villalba of Promigas are at 415 psia. It will be very useful to the HCDP project to use the Condumax sensitivity calibration data provided by Mr. Villalba.