ADVANCES IN NATURAL GAS SAMPLING TECHNOLOGY

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INTRODUCTION

The monetary value of natural gas is based on its energy content and volume. The energy content and physical constants utilized in determining its volume are computed from analysis. Therefore correct assessment of the value of natural gas is dependent to a large extent on overall analytical accuracy.

The largest source of analytical error in natural gas is distortion of the composition during sampling. Sampling clean, dry natural gas, which is well above its Hydrocarbon Dew Point (HCDP) temperature is a relatively simple task. However, sampling natural gas that is at, near, or below its HCDP temperature is challenging. For these reasons, much attention is being focused on proper methods for sampling natural gas which have a high HCDP temperature.

This presentation will address problems associated with sampling natural gas which is at, near, or below its HCDP temperature. Various approaches for solving these problems will also be discussed.

DEFINING THE PROBLEMS

The following is a list of some major problems associated with proper sampling of natural gas:

a. Lack of consensus in the industry as to what constitutes a "representative" sample.

b. Lack of distinction between the sources of liquid, which may be present in some natural gas samples (i.e.-liquid entrained in the source gas versus liquid resulting from condensation in the sample system).

c. Many key personnel involved in sampling of natural gas lack understanding of "Phase Behavior".

d. Misapplication of hardware.

e. Underutilization of available hardware and software which are designed to help solve sampling problems.

LACK OF INDUSTRY CONSENSUS

The key difference of opinion between producers and transporters of natural gas lies in the treatment of liquid entrained in some natural gas streams.

Producers typically would like for natural gas samples to represent in some way the presence of the entrained liquid. They contend that to exclude the liquid is not proper since it was present when the gas volume was measured and represents a source of high energy (and monetary) value.

The transporters typically contend that the entrained liquid presents operational problems that result in increased expenses instead of increased profits.

Industry standards or guidelines do not totally agree on proper methods of sampling natural gas containing entrained liquid. They are not to be blamed because it is a very complex issue requiring substantial research. To the author's knowledge, sampling gas having entrained liquid is not even in the scope of the three major "Industry Standards".

## LACK OF DISTINCTION BETWEEN THE TWO SOURCES OF LIQUID

The origin of liquid found in any natural gas sample system, sample container, or analyzer may be either the result of liquid, which was entrained in the source gas, or condensation that occurred during the sampling process. Before the liquid is eliminated, precautions should be taken to correctly identify its origin. Otherwise serious distortion of the sample's composition could result if the liquid is eliminated incorrectly. In order to fully appreciate why this is so, the relationship between a gas and liquid mixture which are in intimate contact must be reviewed.

VAPOR/LIQUID EQUILIBRIUM

When a gas and a liquid consisting of a *single component* are in intimate contact at a given pressure and temperature for a period of time, equilibrium is attained (See figure #1). When that occurs, the gas phase is saturated with the liquid vapor. The gas phase is also at its dew point temperature. An increase in temperature or a decrease in pressure will result in additional liquid vaporizing thereby increasing its concentration in the gas phase. If the temperature is decreased or the pressure is increased, some of the vapor will condense and return to the liquid phase causing a decrease in its concentration in the gas phase.

Figure #1: "Gas and a liquid equilibrium"
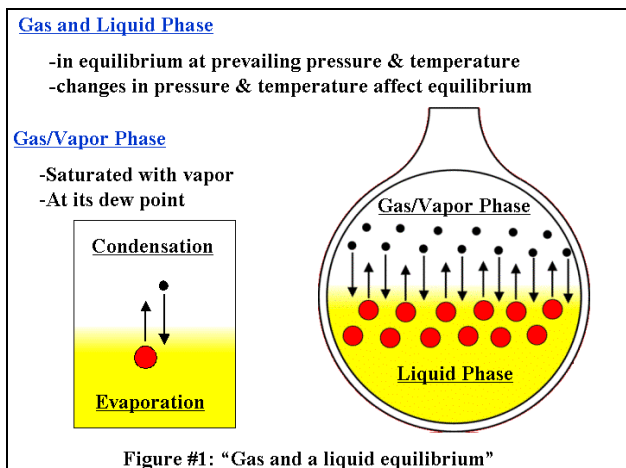
A second example is when a gas and a liquid consisting of *multiple components* are in intimate contact and equilibrated at a given pressure and temperature. Each component of the liquid mixture will vaporize to some degree into the gas phase (See figure #2). The amount of vapor contributed by each liquid at that condition depends upon its concentration in the liquid phase and its volatility.

Figure # 2 "Gases and a mixture of liquids in equilibrium"
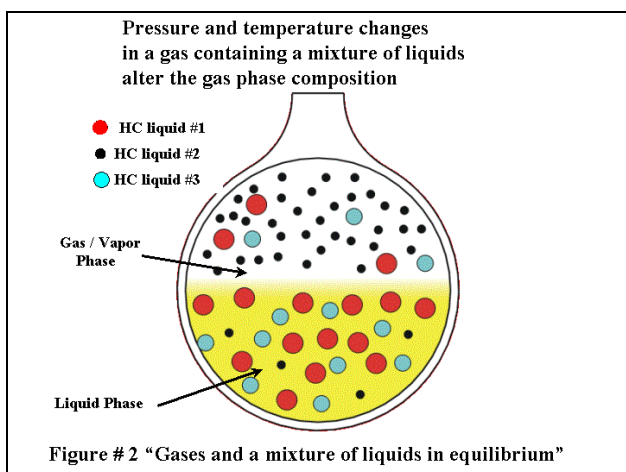
If the gas and liquid mixture temperature is increased and/or its pressure is decreased, some of the liquid mixture will vaporize thereby increasing the concentration of each liquid component in the gas phase (See figure #3). Since the volatility of each component varies, their concentrations in the gas phase will not increase in direct proportion to their concentration in the liquid phase. The net result is that the vapor concentrations of all liquid components will increase in the gas phase. The more volatile components will increase in greater proportion then the less volatile components. Therefore, not only will there be an increase of all liquid component

concentrations in the gas phase, but their ratios will also shift.

Figure# 3: "Effect of Decreasing Pressure or Increasing Temperature
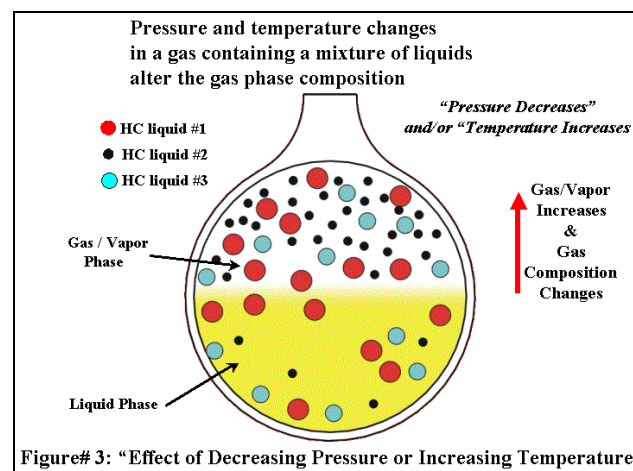
If the gas and liquid temperature is decreased and/or the pressure is increased, the opposite occurs. Some of the liquid vapor components of the gas phase will condense thereby decreasing their concentration in the gas phase (See figure #4). Components will not condense in equal proportions; therefore their ratio in the gas phase will also shift.

Figure# 4: "Effect of Increasing Pressure or Decreasing Temperature
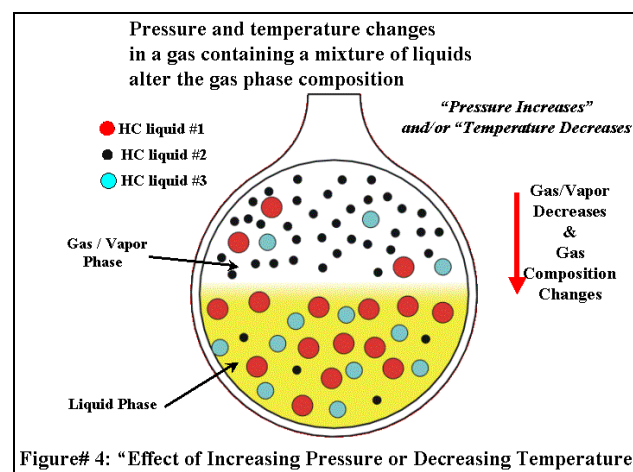
It can therefore be stated that *when liquid is present* in a natural gas sample, a change in either the temperature and/or the pressure will result in a change of the gas phase composition.

For this reason, it is imperative that liquid is removed at the prevailing pressure and temperature condition of the source gas. This is best accomplished inside of the pipeline before the gas enters the sample system. Sampling in that manner will provide a   sample

representing the gas phase composition of the source at its prevailing pressure and temperature.

Liquid removed downstream of pressure regulation should only be for protection of an analyzer since the gas phase composition will not be the same as that of the source gas.

The gas phase composition will also be distorted if hardware is utilized to separate liquids from natural gas samples at a temperature other than that of the pipeline.

In situations where the source gas _does not_ contain entrained liquid, the traditional methods of preventing condensation are applicable. These methods are pressure reduction to lower the HCDP and/or heat tracing to maintain sample conditioning hardware above the sample's HCDP.

LACK OF UNDERSTANDING OF "PHASE BEHAVIOR"

From the preceding discussion, it can be seen that having a working knowledge of "Phase Behavior" is a must for those involved in the sampling of natural gas. This is particularly important when sampling sources which have either entrained hydrocarbon liquids, or when the source gas is near its HCDP temperature, or takes place in low ambient temperature environments.

MISAPPLICATION OF HARDWARE

Some methods and/or hardware designed for _liquid free_ gas sources will likely distort the sample composition when liquid is present in the source gas.

It should be noted that traditional open bore sample probes are not suited for eliminating suspended liquid aerosol droplets from entering the gas sample system.

Probe regulators that do not exclude liquid before regulating the gas pressure can distort the gas composition when liquid is entrained in the source gas. Sintered metal or glass fiber filters are typically utilized to coalesce liquid droplets as the gas flows _through_ the element. What is required however is rejection, not coalescing, of liquid from the gas at the _upstream element surface_ before gas flows through the element. To the author's knowledge, only a phase separation membrane can reject liquid at its upstream surface. Hardware employing phase separating membrane is commercially available to properly precondition gas entering the sample system from a source gas containing liquids.

TOOLS FOR DESIGNING, TROUBLESHOOTING AND EVALUATION OF SAMPLE SYSTEMS.

From the preceding discussions, it can be seen that it is important to know the sample gas and pipeline gas HCDP temperature. The HCDP temperature can be determined either empirically with a chilled mirror device or by calculation utilizing an Equation of State (EOS) Software package.

A chilled mirror HCDP temperature determination is performed at a specific pressure. Whereas this may be suitable in determining if contractual obligations have been met it does not provide all of the information one needs when sampling natural gas. For example, the chilled mirror method does not give insight as to how much liquid will condense when the gas temperature is lower than the HCDP temperature. Also it cannot predict what the HCDP will be at other than the test pressure. These two types of information, which the chilled mirror method does not provide, are very useful in designing, troubleshooting and validating sample systems in natural gas service.

An EOS software package on the other hand can provide a wide range of useful information. From the composition of a specific gas stream the software can perform the following tasks:

- Plot a phase diagram.

- Calculate physical properties which are needed to determine pipeline flow rates (volume).

- Predict if condensation of gas phase components will occur after changing the pressure and/or gas temperature.

- If condensation does occur, predict the amount of liquid which will result and its composition, heat value, and physical properties.

- Predict the change in gas phase composition after condensation occurs.

The following slides are examples of how the previously described tasks are performed by EOS software.
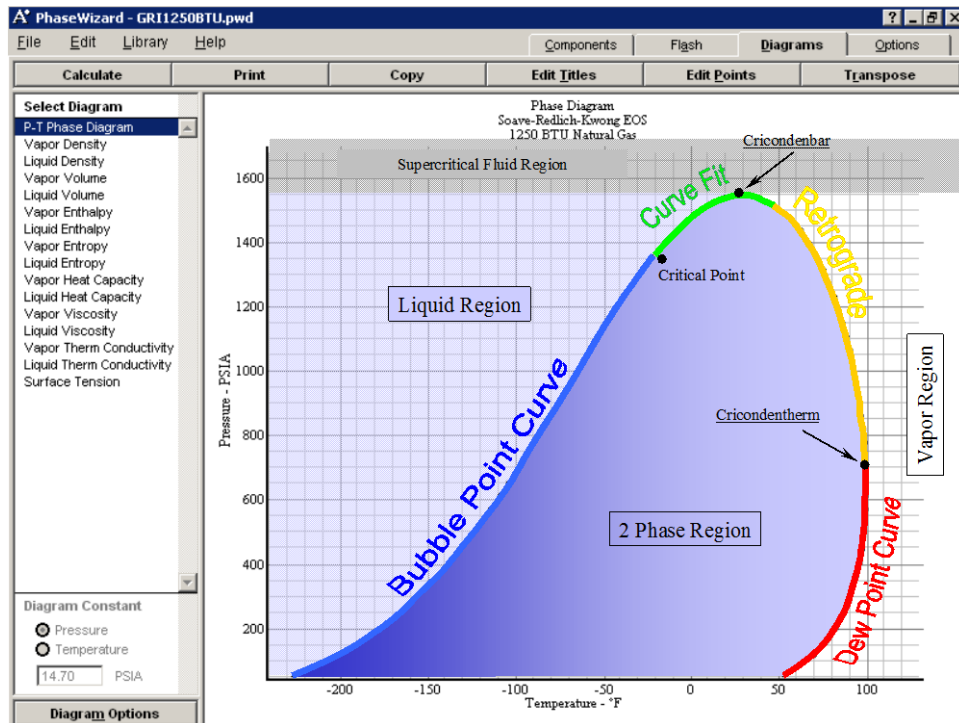
First step is to enter a gas composition

A phase diagram can now be plotted.

Phase Diagram
Soave-Redlich-Kwong EOS
1250 BTU Natural Gas

Physical properties and heat of combustion are calculated.

Stream Properties	Inlet
Condition	Saturated
Percent of Feed - molar	100
Percent Vapor - molar	100
Pressure - PSIA	400
Temperature - °F	94.35
Volume - ft3/lb	0.6373
Density - lb/ft3	1.569
Z Factor	0.9224
Average Mol Wgt	21.484
Enthalpy - BTU/lb	63.939
Entropy - BTU/lb-°F	2.14
Heat Capacity - BTU/lb-°F	0.4915
Viscosity - centipoise	0.0106
Thermal Conductivity - BTU/ft-°F	0.0296
Critical Temperature - °F	-17.18
Critical Pressure - PSIA	1352.53
Heat of combustion (BTU/SCF)	1246.2

Result of reducing the gas pressure under adiabatic (zero heat transfer) conditions.

PhaseWizard Data Sheet
Soave-Redlich-Kwong EOS
Adiabatic Flash 1250 BTU Natural Gas

SATURATED VAPOR

INLET CONDITIONS:
Pres: 400.00 PSIA
Temp: 94.37 °F
'Vapor: 100.000 %

SATURATED VAPOR

Autarchic
Isothermal
Isobaric
Adiabatic

FLASH CONDITIONS:
Pres: 30.00 PSIA
Temp: 74.64 °F
*Vapor: 100.000 %

Heat = 0.000 BTU/lb

Specified Properties
Calculated Properties
* Percent vapor is dry basis

NO LIQUID PHASE

Stream Properties	Original Composition	Composition after pressure reduction	
	Inlet	Vapor	Liquid
Condition	Saturated	Saturated	Empty
Heat of Combustion (BTU/SCF)	1246.2	1246.2	
Methane	75	75	
Ethane	12.5	12.5	
Propane	6	6	
Isobutane	1	1	
n-Butane	1.6	1.6	
Isopentane	0.18	0.18	
n-Pentane	0.24	0.24	
n-Hexane	0.146	0.146	
n-Heptane	0.068	0.068	
n-Octane	0.048	0.048	
n-Nonane	0.012	0.012	
n-Decane	0.006	0.006	
Carbon Dioxide	0.4	0.4	
Nitrogen	2.8	2.8	
Total	100	100	

Result of reducing the temperature under isobaric (constant pressure) conditions.

	Original composition	Composition after temperature reduction	
Stream Properties	Inlet	Vapor	Liquid
Condition	Saturated	Saturated	Saturated
Heat of Combustion (BTU/SCF)	1246.2	1237.1	3529.7
Component Mole Percents			
Methane	75	75.2486	12.31
Ethane	12.5	12.5081	10.4597
Propane	6	5.9592	16.2865
Isobutane	1	0.9796	6.1437
n-Butane	1.6	1.5516	13.7993
Isopentane	0.18	0.1667	3.5277
n-Pentane	0.24	0.2173	5.9689
n-Hexane	0.146	0.1096	9.3324
n-Heptane	0.068	0.0343	8.5715
n-Octane	0.048	0.0125	8.9981
n-Nonane	0.012	0.0013	2.7084
n-Decane	0.006	0.0002	1.457
Carbon Dioxide	0.4	0.4005	0.264
Nitrogen	2.8	2.8104	0.1728
Total	100	100	100

The following are examples of how information generated by the EOS software can be utilized.

- From the gas composition obtained by gas chromatographic analysis determine if liquid was

entrained from the pipeline into the sample system.

- Determine if condensation of sample gas will occur in unheated systems at various ambient temperature conditions and if so, the impact on the BTU and physical property determination.

- Validate the spot sampling method utilized for a specific application.

- Fine tuning sample system operating parameters to insure that the sample gas composition is not altered.

- Determine the impact of pressure and/or temperature changes on the composition, heating value, and physical properties of a natural gas stream.

There are many other uses for EOS software. There are several software packages currently available on the market today. They vary widely in cost and capability.

EOS software has been available for a long time but it has been used primarily for process application. It is only during the recent past that it is being evaluated as a serious tool for analytical applications.

CONCLUSION

Proper Sampling of natural gas is an important element in determining its monetary value. Significant analysis errors can occur when hydrocarbon liquids are entrained in the source, or when the source gas is at or near its HCDP temperature, or when sampling occurs at low ambient temperatures.

The traditional uses of heat tracing and/or gas pressure reduction are appropriate means of preventing condensation. However, applying these traditional solutions for preventing condensation when hydrocarbon liquid is already present in the source gas will result in gas phase distortion.

It is very important to determine the source of liquid to be eliminated before implementing a means for eliminating it. Liquid removed _after_ either the pressure or temperature is changed will alter the gas phase composition. When the source gas contains entrained hydrocarbon liquid, an ideal solution is to utilize hardware designed to remove it inside of the pipeline before pressure or temperature changes occur.

A promising new tool for use in designing, operating, and troubleshooting sample systems is EOS software.