

CONSIDERATIONS FOR SAMPLING WET, HIGH PRESSURE, AND SUPERCRITICAL NATURAL GAS

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Abstract

This paper discusses the problems encountered when sampling wet, high pressure and supercritical natural gas for “on-line” BTU analysis, and provides solutions and comments on how they relate to the API and GPA industry standards for natural gas sampling. It also discusses the use of phase diagrams in the design and operation of a natural gas sampling system.

Introduction

It is a well established fact that the sample conditioning system (SCS) is the largest source of error in natural gas analysis. The SCS is comprised of all the components which contact the sample on its journey to the analyzer, including those which are designed to protect the analyzer from damage by solids and liquids. Its purpose is to extract a representative sample from a natural gas source, condition it so that it is compatible with the analyzer, then transport it to the analyzer for analysis. During this process, the SCS must maintain the integrity of the sample composition.

Knowledge of the physics and chemistry related to the extraction, transportation and conditioning of natural gas sampling is a must for anyone who designs, maintains, or purchases a sample conditioning system.

Defining a “Representative” Sample

The first step in sampling natural gas is the extraction process. It consists of removing a small, continuously flowing stream of the gas, representative of the source, and transporting it to an analyzer. This step is where the most severe problems are encountered. To make matters worse, not everyone agrees on the definition of “representative” when sampling natural gas. Additionally the industry standards are not absolutely clear on what is considered a “representative” sample. As a matter of fact, there is no industry standard which covers the sampling of wet gases. The standard most applicable to “on-line” sampling of natural gas by gas chromatography (GC) is the American Petroleum Institute (API) Chapter 14.1. The following are direct quotes from its Section 2: Purpose and Scope:

“The purpose of this standard is to provide a comprehensive guideline for properly collecting, conditioning and handling representative samples of

natural gas that are at or above their hydrocarbon dew point.”

“This standard does not include sampling multi-phase flow (free liquid and gas) or supercritical fluids.”

The term “multi-phase flow” is defined as “two or more phases in the stream” (Section 4.19 of API Chapter 14.1). In Section 4.26 of this standard, the term “representative gas sample” is defined as “compositionally identical or near to identical as possible to the sample source stream.”

One would think that the scope and definition of terms in these standards would make clear what it considers a “representative sample” of natural gas; however, the author frequently encounters individuals who contend that mist and aerosol liquid is not “free liquid” and therefore should be included in the gas sample.

There is a lack of clear consensus in the industry as to what constitutes a representative sample when mist or aerosol liquid is present in the gas source. It could be settled by adding language to the API 14.1 standard which clearly excludes all forms of liquid. Until then it is safe to assume that the standard does not apply to gas that has any entrained liquid, even small aerosol liquid particles since all forms of liquid exhibit the same physical and chemical characteristics.

For the purpose of this paper the author defines a representative sample, when liquids are present in the source gas, as consisting of only the gas phase at the prevailing pressure and temperature of the source gas at the point of sampling. This view is supported by the API 14.1 standard Appendix B; Section B.3 “Multi-phase flow”. It states, in summary, that current sampling technology is not sufficiently advanced to obtain a sample representing both phases.

Problems Encountered When Sampling and Conditioning Wet, High Pressure, or Supercritical Natural Gas

The first problem is how to extract a “representative” sample when liquid in any form is present in the source gas. The solution to this problem is to exclude the liquid at prevailing source gas pressure and temperature. This certainly entails liquid exclusion “inside” of the pipeline.

This is best accomplished with a probe having a phase separating membrane integrated in the sample probe entrance. It is not practical to maintain line conditions to an external location for liquid separation. If pressure regulation and/or temperature changes occur before liquid is removed the gas phase will be distorted and will no longer be “representative”.

The second problem is extracting a representative sample from a high pressure natural gas source, even though it does not contain entrained liquid. The first steps towards a solution are to determine the type of sample probe that should be used, whether internal or external pressure regulation is required, and if heating is required. In order to make these determinations it is necessary to utilize a phase diagram for the gas composition to be extracted.

Natural Gas Phase Diagrams

A phase diagram is a graph which shows the gas/liquid phase relationships at various pressure and temperature conditions. The phase diagram of Figure 1 is of a typical natural gas composition in the 1250 BTU range. The parts of the phase diagram in Figure 1 are referenced below:

1. The critical point (B) is the pressure and temperature conditions where a phase boundary ceases to exist.
2. The cricondenbar (C) is the highest pressure point on the phase envelope.
3. The cricondentherm (D) is the highest temperature point on the phase envelope.
4. Line A-B is the section of the phase diagram known as the bubble point curve.
5. Line D-E is the section of the phase diagram known as the dew point curve.
6. Line C-D is usually referred to as the retrograde dew point curve.
7. The area to the left of the phase envelope and below the critical point is the liquid phase.
8. The area to the right of the phase envelope and below the critical point is the gas phase.
9. The area underneath the phase envelope is the “multi-phase” region
10. The area above and to the right of the critical point is the “supercritical fluid”. This fluid is neither gas nor liquid.

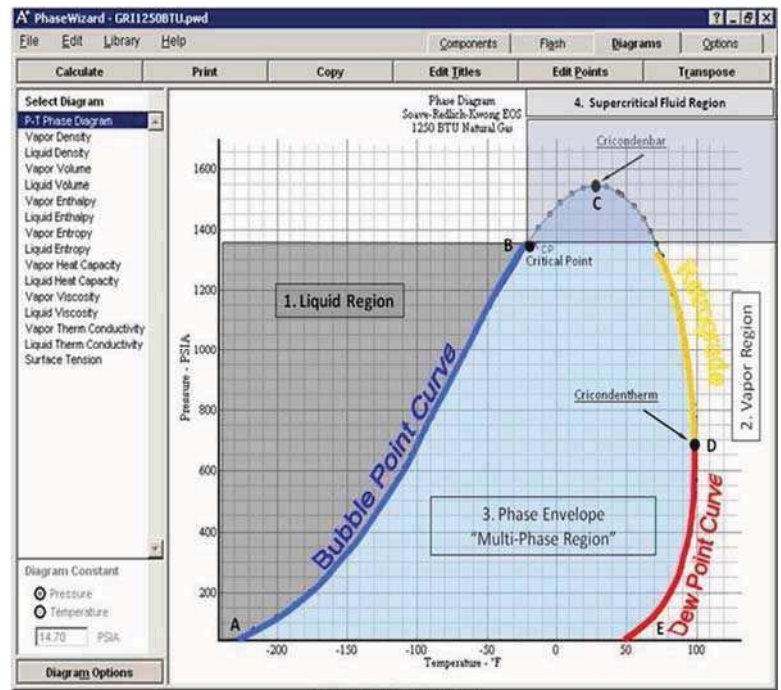


Figure 1

Sampling a “High Pressure” Natural Gas Source

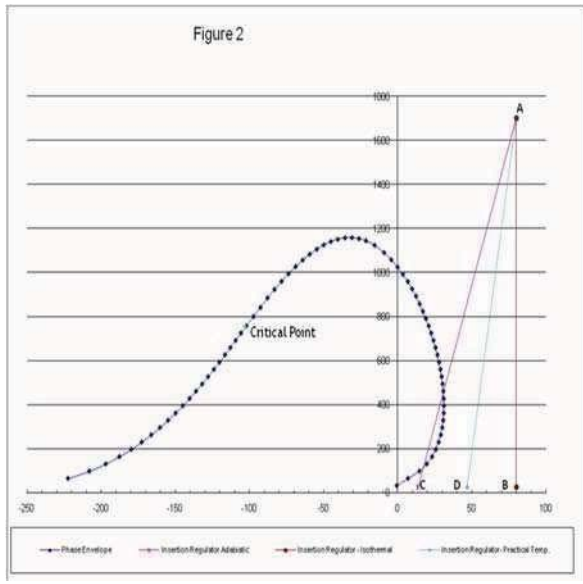
For the following discussion, refer to Figure 2: The source gas pressure and temperature conditions are represented by Point (A). Point (C) represents the temperature after an adiabatic (no heat transfer) pressure drop. Point (B) represents the temperature after an isothermal (without temperature change) pressure reduction. Point (D) represents the actual (practical) temperature after a pressure reduction with a typical insertion regulator.

Note that insertion pressure regulators are designed to “offset” or prevent excessive Joule-Thomson (J-T) cooling during pressure reduction. This is accomplished by having the pressure reduction valve located in a section of the sample probe which is inside of the pipeline. This allows the sample gas to be “heat sunk” to the process gas thereby preventing an adiabatic condition. Since it is not a 100% effective process the actual temperature lies somewhere between the isothermal and adiabatic temperature points.

Experience has shown the “practical” temperature point to be near the midpoint of the adiabatic and isothermal temperature points. The “practical” temperature point will be used in this discussion for guidance in the design and operation of sample systems.

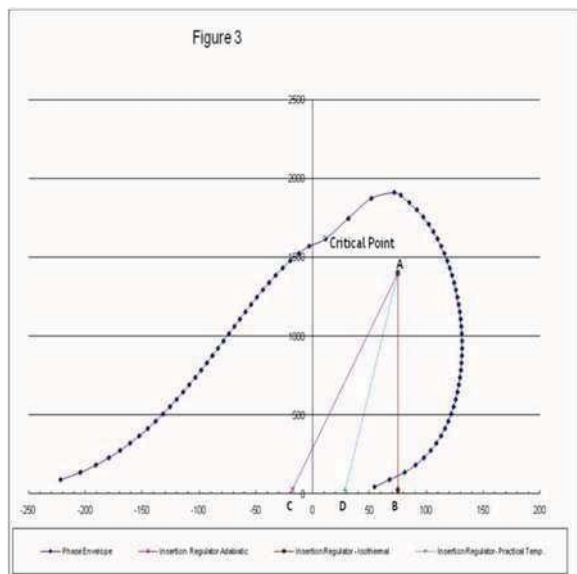
In figure 2, line A-B represents an isothermal pressure reduction from 1700 PSI to 25 PSI. Line A-C represents an adiabatic pressure drop of the same magnitude. Line A-D represents the actual, “practical” temperature/pressure condition obtained with an insertion regulator. Thus it can be seen that by using an insertion pressure regulator (line A-D) the phase envelope is not traversed during the pressure reduction. If a

temperature/pressure condition point were to enter the phase envelope area during pressure reduction, then sample distortion would likely occur. For an external pressure regulator to be used successfully in this case, the ambient temperature would have to transfer enough heat to maintain the regulator at least 30°F above the cricondenthem temperature in order to conform with the API 14.1 standard. The standard requires that the sample gas be maintained a minimum of 30°F above its hydrocarbon dew point (HCDP) at all times. This is due to the uncertainty of the HCDP determination.



Sampling a “Wet” Natural Gas Source

The term “wet” in natural gas parlance means natural gas containing liquid of any type. In referring to Figure 3, it can be seen that source conditions of 1400 PSI and 75°F, represented by point (A), are within the phase envelope and therefore the source gas has some entrained liquid.



Current sampling technology cannot assure the extraction of a sample containing a representative amount of both phases. The practical approach is to exclude the liquid at line conditions. Therefore a phase separation membrane tipped probe is recommended for this application.

Since the membrane will exclude the liquids, a new phase diagram is plotted (Figure 4) using only the gas phase composition. Point (A) of Figure 4 (1400 PSI and 75°F) is on the phase boundary and therefore is in a saturated condition. In referring to Figure 4, it can be seen that “practical” temperature/pressure line A-D of an insertion regulator traverses the phase envelope and will result in condensation, which would distort the sample composition. In order to prevent condensation, it is necessary to heat the sample before pressure reduction and maintain the sample temperature a minimum of 30°F above the cricondenthem temperature during pressure reduction.

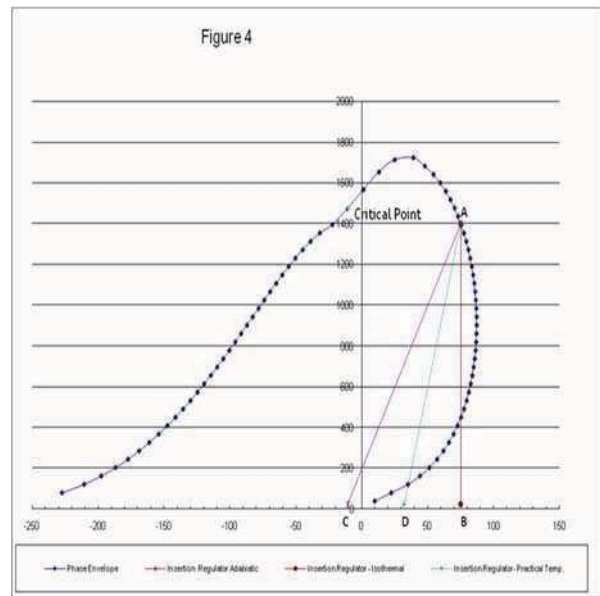
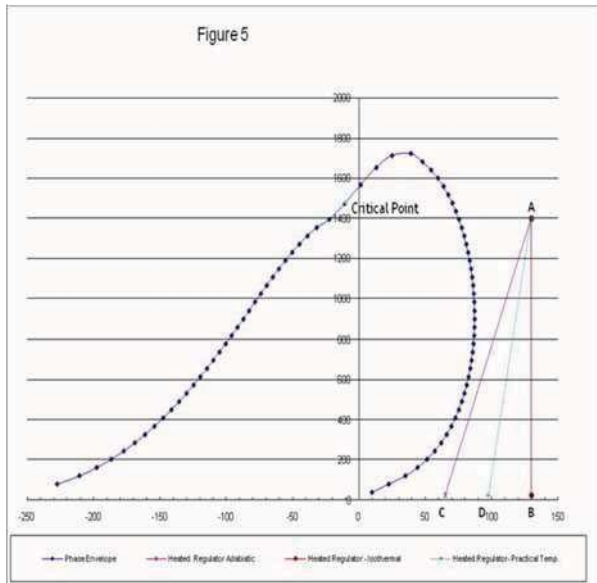
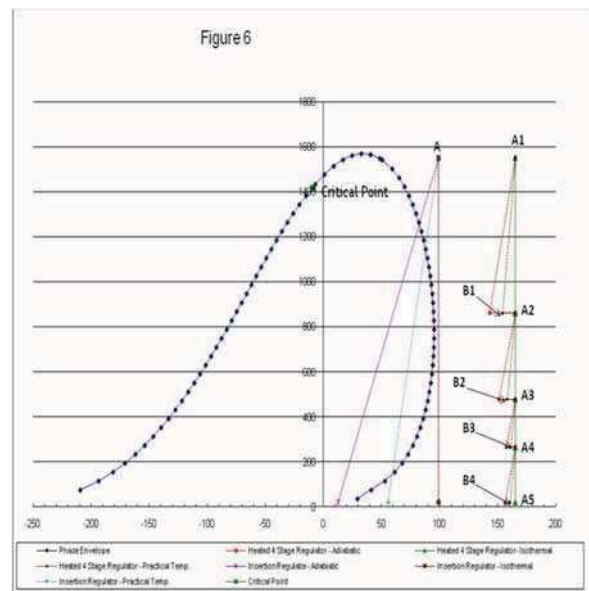


Figure 5 below is the same phase diagram as seen in Figure 4; however, it depicts pressure reduction with a heated regulator. The “practical temperature/pressure” line A-D of the heated regulator does not traverse the phase envelope and should be used to determine heating requirements.



Sampling Natural Gas in a Supercritical Condition

The source temperature and pressure condition (Point A) of the natural gas composition in Figure 6 places it in the “supercritical” area of the graph. It can be seen that any pressure reduction without heating will cause the sample to traverse the phase envelope and will more than likely cause severe sample distortion. This condition causes pressure surging in single stage insertion pressure regulators and erratic analytical results. The author’s recommendation is to extract the sample under conditions which will ensure that pressure and temperature changes do not allow the sample to change from its supercritical state. Next, transfer the sample to an external regulator through a sample line heated at least 30°F above the cricondentherm temperature. Multiple stages of pressure regulation, with reheating of the sample gas between stages is recommended. Points A1, A2, A3, A4, and A5 represent the temperature/pressure points after reheating four stages of pressure reduction. Points B1, B2, B3, and B4 represent the actual, “practical” temperature after each pressure reduction stage.



The recommendations made in this paper are all based on experience in similar circumstances. The sample extraction process for high pressure, wet, or supercritical gases is the most critical step in the analytical process. If this step is not performed correctly, then the sample gas analysis will be invalid.

Transporting the sample to an analyzer

The sample must be kept at least 30°F above its HCDP temperature until it is injected into the Gas Chromatograph.

Summary

Designing a sample system for natural gas sources which are at or below their HCDP temperature or in a supercritical state requires careful attention and a basic knowledge of thermodynamics. The API 14.1 standard is a good reference even though its scope is limited to source gas which is at or above its HCDP temperature. The use of an “Equation of State” software program is a must for making decisions when extracting natural gas under the difficult conditions discussed in this paper.