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# **CONSIDERATIONS IN SAMPLING WET, HIGH PRESSURE OR SUPERCRITICAL NATURAL GAS**

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## **Introduction**

This paper discusses the problems encountered during online sampling of wet, high pressure and supercritical natural gas for subsequent compositional analysis. It provides solutions and comments on how they relate to the API and GPA industry standards for natural gas sampling. The paper also discusses the use of phase diagrams in the design and operation of a natural gas sampling system.

The phase diagrams presented in this paper were calculated using a commercial software program intended for that purpose. The Peng-Robinson Equation of state was utilized by the software to compute pressures and temperatures necessary to construct each phase diagram presented. The gas compositions considered in this document were either taken from AGA Report 8<sup>1</sup> or from actual gas sample analyses. The Joule Thomson coefficient was calculated from a molar gas analysis using Refprop 23 version 9.0 which is available from NIST<sup>2</sup>.

The term "wet gas" as used in this paper refers to a flowing natural gas stream, having both a vapor and liquid phase at equilibrium conditions determined by pipeline conditions. The gas is assumed to have been dehydrated and has a water content of less than 7 pounds per million standard cubic feet of gas.

The applicable standards for sampling natural gas are API MPMS 14.1<sup>3</sup> and GPA 2166-05<sup>4</sup>. These standards are quite clear in that they are only applicable to the sampling of natural gas mixtures which are in the vapor phase. Flowing gas streams which are at hydrocarbon dew point temperature, or are exposed to piping elements that are below the dew point temperature, pose significant challenges for on-line sampling equipment operation and may generate custody transfer settlement or gas quality arguments between contracting parties.

## **Representative Samples**

The objective of natural gas sampling is to obtain a sample which is representative of the bulk characteristics of the gas mixture. Spot sampling will only yield a sample that is representative of the composition at that particular instant in time.

Long term proportional-to-flow sampling methods such as automatic composite samplers and on-line gas chromatographs will give analytical results which are significantly more representative over time than spot sampling. However, the equipment for both of these systems can be fouled and made inoperable by liquid contamination of their respective sampling systems.

It is difficult to accurately apply the term "representative" when one considers the occurrence of gas condensation within the pipe. Given that the objective is to sample the gas and perform a compositional analysis of that sample, when components of the gas begin to condense they have a tendency to drop out of the vapor phase and adhere or adsorb to the surface of the pipe<sup>5,6</sup>. In this condition a fraction of the gas has now been removed from the flowing stream and may not be available for delivery to the sample probe. This can lead to a gas sample which has a reduced fraction of "heavy" hydrocarbon components such as Pentanes, Hexanes, etc.

As the condensation process continues the droplets begin to stream along the walls of the pipe. This can lead to the pooling of liquids at low velocity points within the piping, or possibly the delivery of droplets to the tip of the sample probe. These droplets are referred to as "free" liquids. The inclusion of free liquids in the sample may bias the sample richer than is truly representative of the original gas composition if it has a disproportionate fraction of heavy hydrocarbon components. The biasing may affect the gas heating value and calculated hydrocarbon dew point.

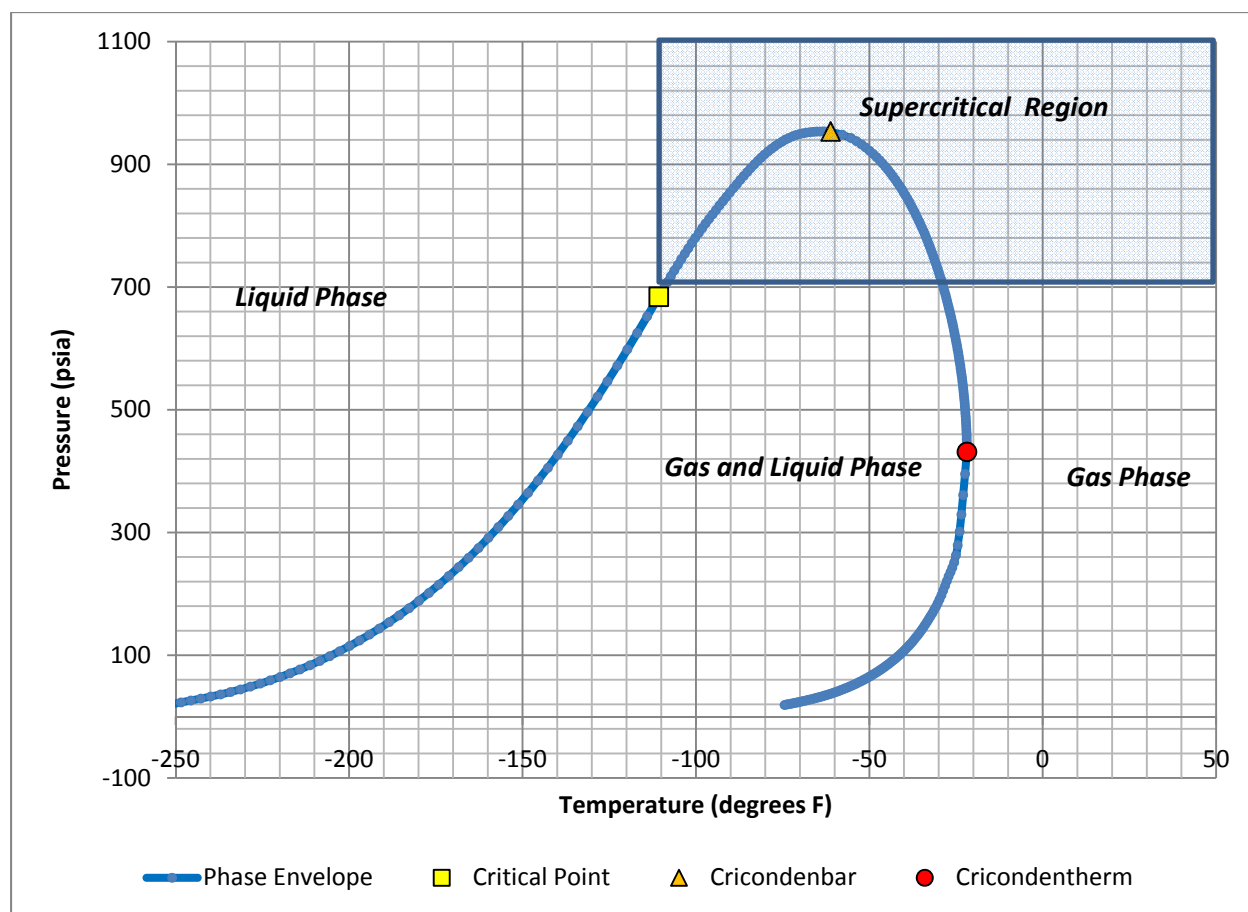
## Phase Diagrams

In order to understand this phase change phenomenon it is useful to study calculated phase diagrams generated by cubic equations of state. Commonly utilized cubic equations of state are the Peng-Robinson and Suave-Redlich-Kwong equations. These equations are used to compute the density of a specified hydrocarbon mixture at a given pressure and temperature. They are particularly useful in determining the pressure and temperature regions at which the mixture, as a vapor, will begin to condense to a liquid. This region of condensation is referred to as the dew point region of the phase envelope.

Figure 1 is an example Pressure Temperature (P–T) phase diagram computed using the Gulf Coast gas composition described in AGA Report 8<sup>1</sup>. The phase envelope is plotted as a function of pressure and temperature.

Three important points along the phase envelope are the critical point, the cricondenbar, and the cricondentherm. The critical point is the location at which the densities of the hydrocarbon liquid and vapor are equal, and the point above which distinct liquid and vapor phases exist. The region directly above and to the left of the phase envelope is the liquid phase. Inside the phase envelope is the two-phase region where the hydrocarbon mixture will have components in both a gas and liquid phase in varying proportions. The cricondenbar is the maximum pressure on the phase envelope at which both phases can co-exist and above which no gas phase can be formed. The cricondentherm on the phase envelope is defined as the highest temperature at which both phases can co-exist and above which no liquids can be generated. So, if a gas mixture is kept above its cricondentherm, it will remain in a vapor phase only, regardless of the pressure.

Figure 1: Two phase P-T plot for “Gulf Coast” gas composition given in AGA Report 8.



The portion of the phase envelope below and to the left of the critical point is referred to as the “bubble point” curve. The bubble point curve is the phase region where saturated liquids begin to form

bubbles” of infinitesimally small amounts of vapor. Pressures and temperatures that would plot above and to the right of the critical point are referred to as supercritical, or above the critical point. The supercritical region is also described as the dense phase region because hydrocarbon density behavior in this region is difficult to describe as gas or liquid only.

The part of the phase envelope to the right of the critical point defining the phase boundary is referred to as the dew point curve. Dew points are conditions at which the first infinitesimal drops of liquid are formed at saturated vapor conditions. Dew points plotted between the cricondenbar and cricondentherm comprise the “retrograde” region of the phase envelope. At pressures and temperatures outside of the phase envelope, to the right of the dew points, is where the hydrocarbon mixture will exist as a gas.

The shape and size of the phase envelope is determined by the composition of the hydrocarbon mixture. Figure 2 is a plot of four different gas compositions on the same P-T plot.

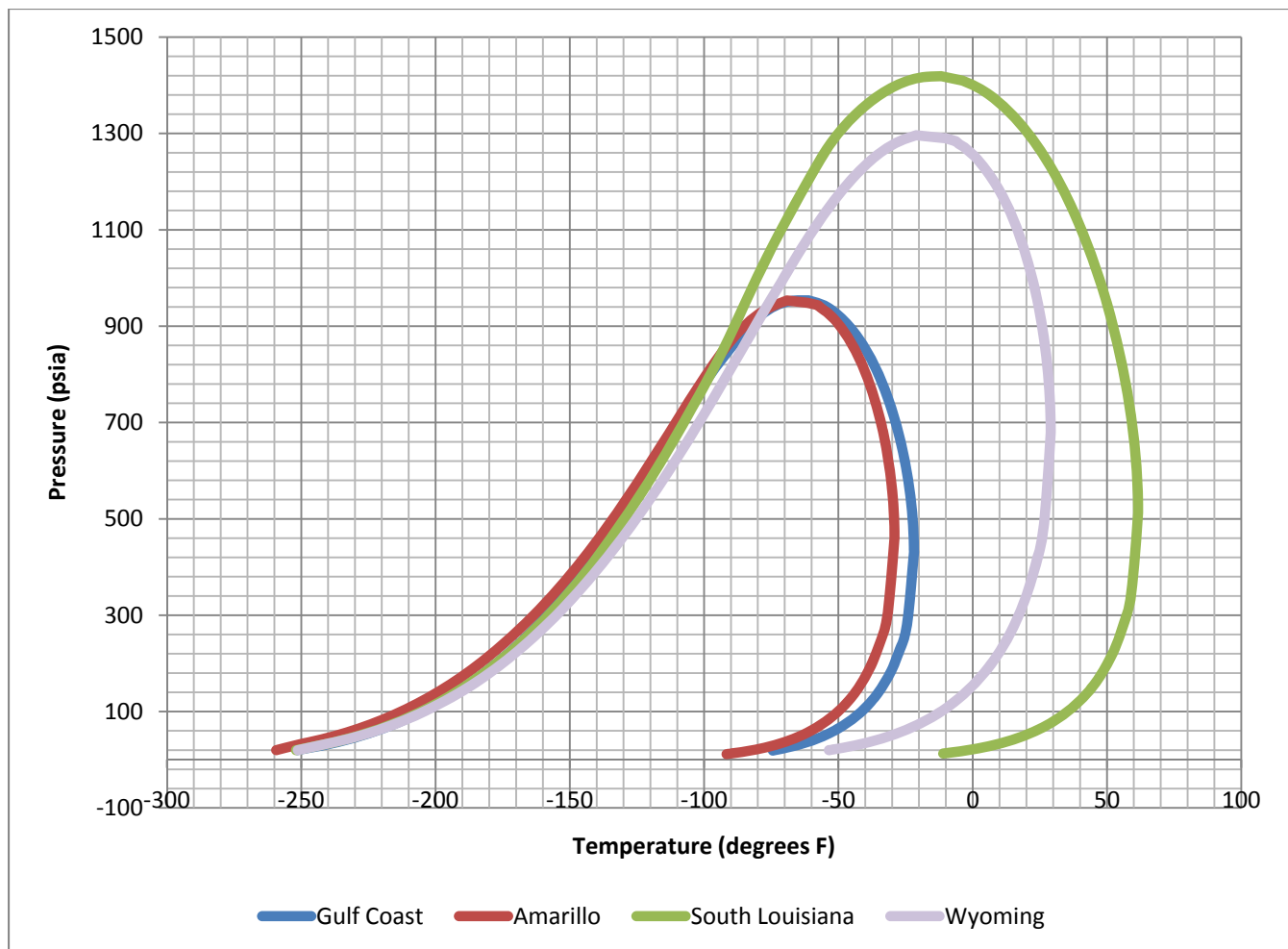


Figure 2: P-T plot of phase diagram for four different gas compositions.

Gas compositions “Gulf Coast” and “Amarillo” do not have as much Pentanes plus fractions as do “Sample A” and “Sample B”. Consequently their two-phase region is smaller, and the opportunity to form liquids only exists at very low temperatures. This is not the case however, for “Sample A” and “Sample B” gases which might be typical of heavy hydrocarbon-rich production gas. Note that liquid condensation is likely to occur at pressures and temperatures at or near pipeline operating conditions.

We will next examine some sample system design considerations and demonstrate how phase diagrams are a useful tool for on-line sampling system design.

### **On-line Sampling System Considerations**

It should be a matter of common sense that if hydrocarbon condensation is expected to occur, then a gas/liquid separator is necessary immediately upstream of the gas meter station. However, as Abraham Lincoln once pointed out, common sense tends not to be so common. In this industry there has been a long history of discussion concerning adverse operating conditions due to free liquids in the flow stream and the impact on flow measurement<sup>7,8,9,10,11</sup>.

It is recommended that sampling be done using sample probes inserted into the center one third of the pipe diameter<sup>3,4</sup>. This will ensure that the point of sample entry is removed from the pipe wall where free liquids might exist. It is also advisable to use a top tap on the pipe to allow the probe to be inserted in the vertical position. Such practice would allow gravity to aid in the draining of free liquids from the sample probe inlet.

The proper placement of sample probes is important to successful gas sampling results. Locations which may generate high turbulence or swirling flow patterns would tend to encourage vaporization of condensed gas fractions from the pipe wall and produce a false enrichment of the gas flow stream. A sample point on the gas meter tube at a point of velocity profile reattachment is the best place to take a sample. Placement near disturbing elements such as flow conditioners and orifice plates in general should be avoided.

It has become industry practice to utilize at the point of sample entry, filters or membranes impermeable to liquids to ensure that only the gas vapor phase is delivered into the sample system<sup>12,13</sup>. This practice is recognized in industry standards as well<sup>4</sup>.

The requirement for successful on-line sample system design is to ensure that at no point along the sample system is there an opportunity for condensation to occur prior to sample delivery into a composite sample cylinder, or to an on-line gas chromatograph. It has been demonstrated that condensation formed after taking the sample, within a sample bottle, is not a concern as long as the sample cylinder has been pre-heated prior to chromatographic analysis in a laboratory<sup>14</sup>. If condensation is allowed to occur on the sample side of a membrane separator it can be expected that sample distortion will occur as described above. Operators must pay attention to manufacturers' instructions concerning the application of membrane separators and filters, as their successful application may be compromised when large pressure gradients are created across these devices. They also may not be appropriate for spot sampling situations.

### **Regulation Staging and Sample System Heating**

On-line chromatographs require a pressure reduction from line pressure to a very low sample stream pressure. This presents a new set of problems for most gas streams, as along with pressure reduction comes the thermodynamic Joule-Thomson cooling effect. This phenomenon may be dealt with by multi-staging the pressure reductions and by heating the gas stream and equipment prior to the pressure cuts. Keep in mind that using phase diagrams as a design tool for the sample system may have a predictive dew point temperature uncertainty of as much as 30°F<sup>3,4</sup>.

Perhaps the best way to discuss the topic of sample system design is by referring to the use of phase diagrams as a visualization tool for sample phase behavior. Figure 3 depicts the phase envelope for a production gas that is being taken either through a series of pressure reductions or a single pressure cut for sampling purposes. Three pressure reduction paths are depicted. The first path begins at 45 degrees F and 800 psia. Using the calculated Joule Thomson (J-T) temperature change for a single idealized adiabatic pressure reduction it is apparent that some portion of the gas will form liquids before reaching the desired chromatograph sample pressure of 30 psia. The use of the term "idealized" in this document is expressing the idea that no other energy losses or sources which might have an influence on the gas temperature have been taken into account.

The second path depicts a single stage reduction through an idealized adiabatic pressure reduction from a beginning temperature of 65 degrees F. This may be satisfactory at certain times in the year, but path one type results may possibly exist at other times in the winter.

The third path demonstrates how the entire pressure cut may be accomplished in three pressure reduction stages. The three reductions stages are from 800 to 500 psia, 500 to 200 psia, and 200 to 30 psia. Heat is added to the gas stream at each stage to maintain a minimum sample temperature of 55 degree F despite J-T

cooling. Note that the pressure reduction is made as a net isothermal pressure reduction since the ending temperature is the same as the beginning temperature.

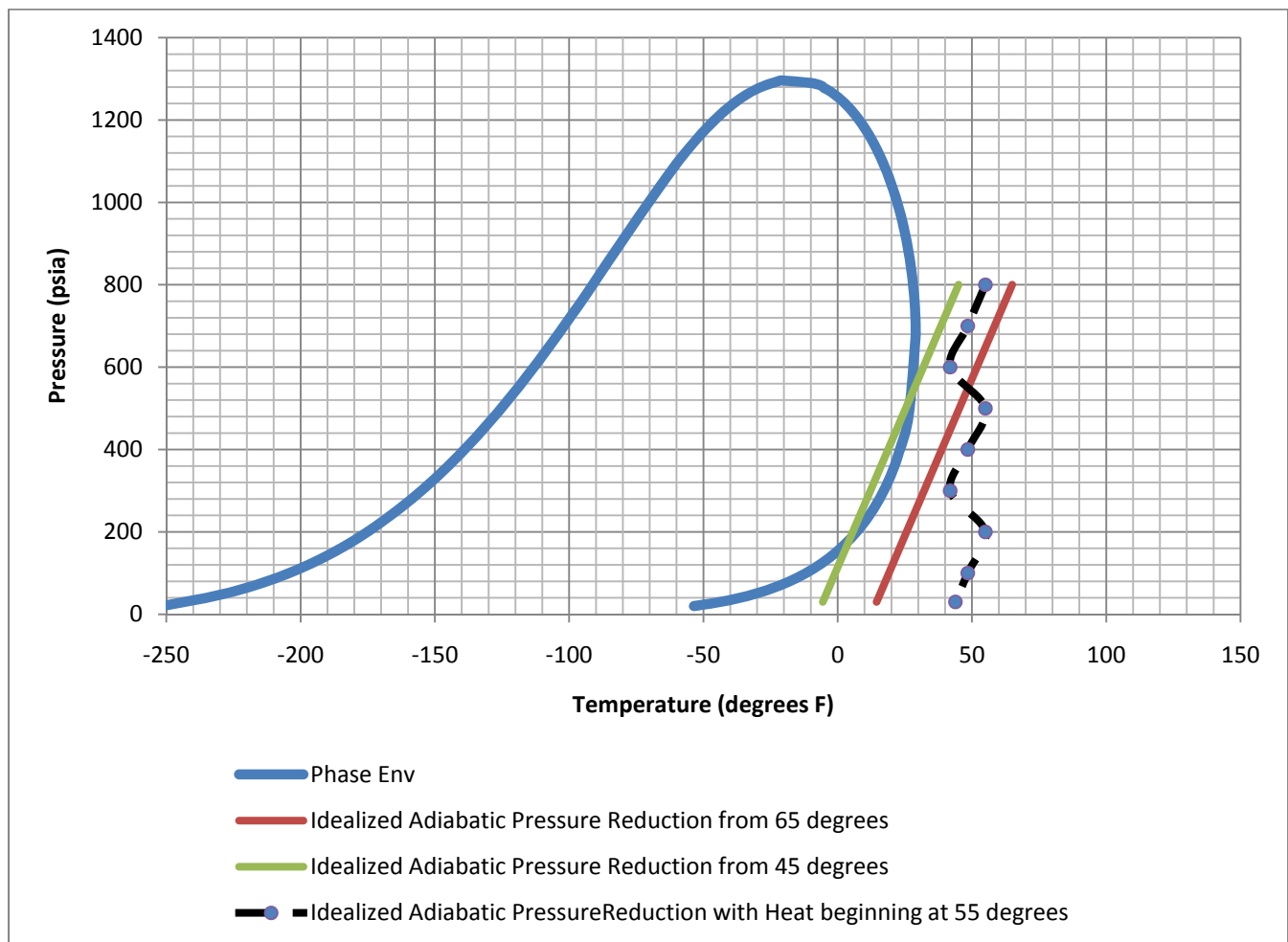


Figure 3: P-T Plot of phase diagram showing pressure reduction paths for gas sampling.

### Supercritical Applications

Supercritical conditions also present challenges for sample system design. However, we should be able to apply some of the lessons learned thus far to this application.

For the treatment of the high pressure reductions needed in supercritical applications heat input to the gas stream is a must. Figure 4 demonstrates three paths to accomplish the necessary pressure cut. One will be most unsatisfactory and the other two are considered practical alternatives.

The first pressure reduction path begins at 45 degrees F and makes one single reduction from 1320- to 30 psia. This will result in a two-phase sample as the reduction path travels through the two-phase region.

The second pressure reduction path begins at the same initial gas conditions as the first, but makes the pressure drop in three stages. The pressure reduction is stepped from 1320 to 1120 psia, then 1120-820 psia, and finally 820 to 30 psia. Temperature is maintained by heating to 65 degrees F at each stage.

The third pressure reduction path begins at the same line pressure but is started at 60 degrees F so that the graph will be easier to read. In this pressure reduction path there are two pressure reduction stages: 1320 to 1020 psia and 1020 to 30 psia. Additional heat is applied to provide an inter-stage temperature of 85 degrees F

before making the final pressure cut. Both the second and the third paths produce the desired result of a low pressure gas sample with no free liquids.

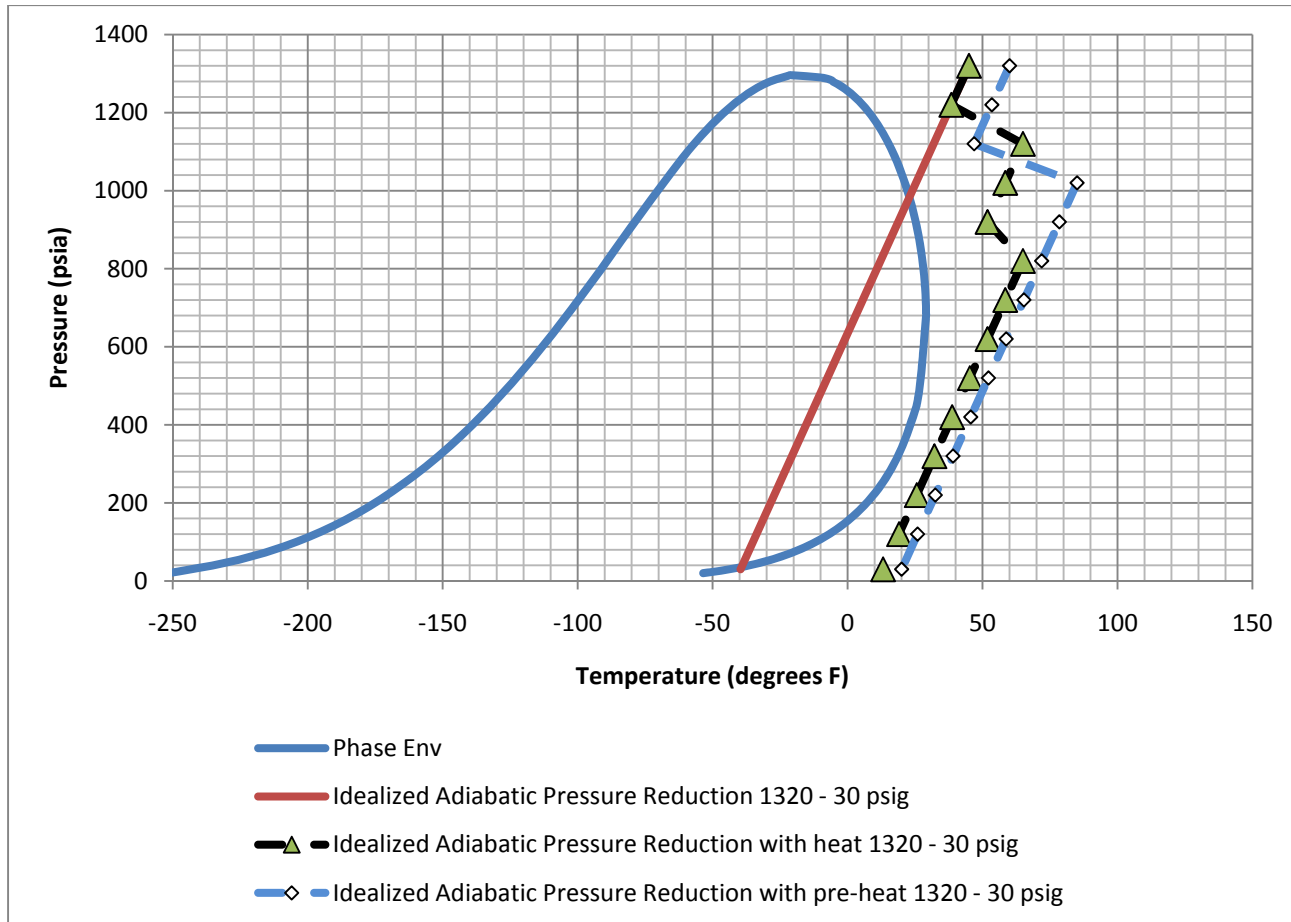


Figure 4: P-T Plot of phase diagram and pressure reduction paths beginning at supercritical line conditions.

## Conclusions

The industry has learned much about how to measure natural gas at both condensing (dew point) and supercritical conditions. There are numerous equipment suppliers which can assist in the design and assembly of a proper sampling system for these and other operating conditions.

It is important that the sample system designer and operator understand the characteristics and phase behavior of the gas stream that will be measured and analyzed for custody transfer purposes. Much more information on the topic of gas sampling exists in the literature, and the reader is encouraged to do their own study to understand the intricacies of gas sampling and its impact on gas measurement.

For two-phase flow, on-line sampling methods have and are being developed. However, the accuracy or overall uncertainty of those methods must first be proven. The current best approach to custody transfer measurement and analysis at such operating conditions is to separate the gas and liquid phases and measure each separately.

## Acknowledgements

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## Appendix

Compositions for gas mixtures used in this paper.

	Gulf Coast	Amarillo	S. Louisiana	Wyoming
Components	Mole %	Mole %	Mole %	Mole %
Methane	96.5222	90.6724	93.9139	86.6296
Ethane	1.8186	4.5279	2.8943	6.9470
Propane	0.4596	0.828	1.1843	2.3997
Isobutane	0.0977	0.1037	0.2915	0.6161
n-Butane	0.1007	0.1563	0.3637	0.8876
Isopentane	0.0473	0.0321	0.1423	0.4317
n-Pentane	0.0324	0.0443	0.1122	0.0000
n-Hexane	0.0664	0.0393	0.2234	0.1054
Carbon Dioxide	0.5956	0.4676	0.2705	1.0690
Nitrogen	0.2595	3.1284	0.6041	0.9140