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BTU Analysis using a Gas Chromatograph

Class # 5020

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Introduction

Prior to 1978, most custody transfer of natural gas contracts were based on the volume of gas being transferred between the parties. In 1978, congress passed the Natural Gas Policy Act that mandated the custody transfer of natural gas based on the energy content, creating the need to determine the energy content of the natural gas at the custody transfer location. An instrument that burnt the gas and measured the heat output of the flame, a *calorimeter*, was then widely used to determine the energy content. In the mid-eighties, the functionality and reliability of gas chromatographs (GC) began to surpass the calorimeter and the GC eventually took over the energy measurement role to become the most common method for determining the energy content of the gas. This paper will provide an overview of the considerations for online measurement of BTU and how the GC calculates the energy content.

The Sample Handling System

The first part of the accurate energy calculation is to take a representative sample of the natural gas flowing through the custody transfer metering point. To take a representative sample, a sample probe is used to avoid any liquid or solids contamination that may be on the pipe wall (Figure 1). The sample probe is best located on the upstream section of the meter run in an area free of excessive turbulence (Figure 2).

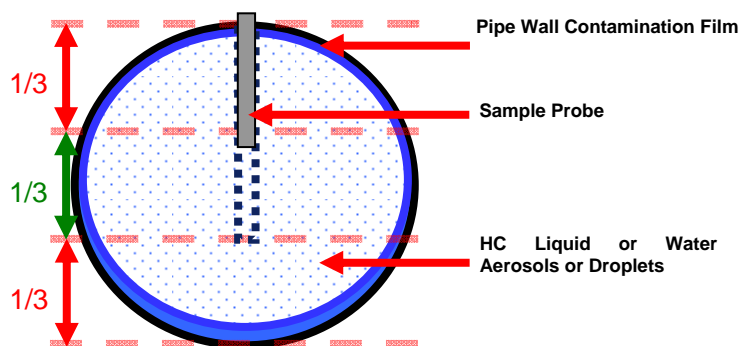


Figure 1 – The sample probe is used to take a sample free of the contamination of liquids and solids found on the pipe wall.

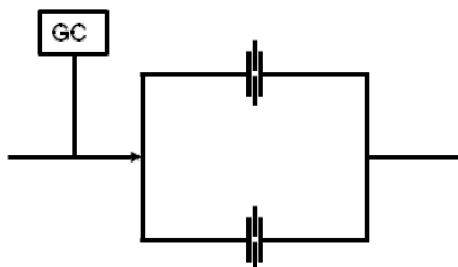


Figure 2 - The recommended sample probe location is on the inlet to the meter runs in an area of low turbulence and to ensure the sample is representative of the gas flowing through both of the meter runs.

The sample is conditioned to remove any liquid or solid contaminants (larger than 2 microns) and the pressure reduced from the pipeline pressure down to between 15 and 30 PSIG (100 to 200 kPaG). When the sample is

conditioned for analysis, the composition of the vapor phase must be maintained. The materials and components of the sample handling system (SHS) are typically stainless steel and or designed specifically for the natural gas application. Copper or plastic tubing and glycol filters should never be used as they will selectively remove some of the components and change the composition of the sample.

When reducing the pressure of the sample, the Joules-Thompson effect will reduce the temperature of the gas. If the temperature drops below the sample's *hydrocarbon dew point*, the heavier hydrocarbons will drop out of the gas phase and form hydrocarbon condensation in the sample system – and change the composition of the sample. Reducing the pressure inside the pipeline (using the heat from the flowing gas to overcome this cooling effect) or using heated regulators to increase the temperature of the sample will avoid this issue.

The sample is transported to the GC through the *sample lines*. The sample lines should be heated to ensure the temperature of the sample is kept above the hydrocarbon dew point. Figure 1 shows an example of how the composition and the calculated energy content is changed if the temperature of the sample drops below the hydrocarbon dew point. The API 14.1 standard recommends the sample should always be kept at least 30 °F (16.6 °C) above the expected hydrocarbon dew point (API 14.1, 2006, Section 6.6) to ensure the composition of the sample is maintained.

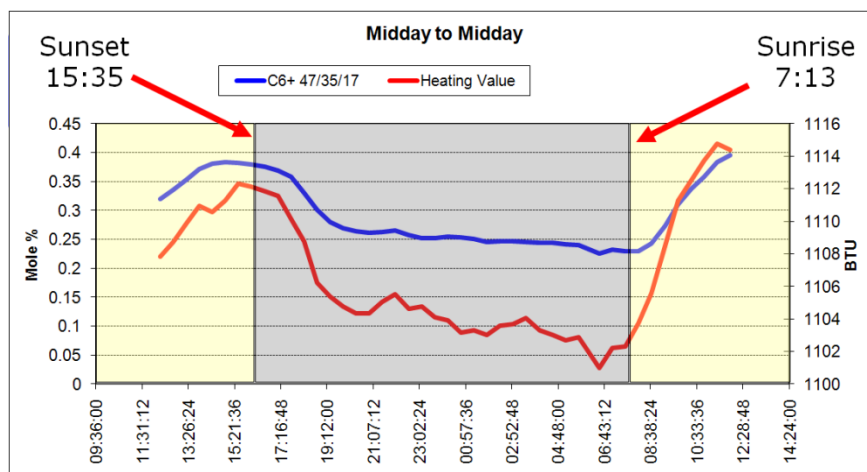


Figure 3 - An example of the composition changing in the sample lines when the ambient temperature drops.

Composition Normalization

The GC measures each of the individual components it is calibrated to measure. When each of the component concentrations is summed, they will usually not add up to 100%. One of the reasons that they will not add up to 100% is the GC is usually configured to look for 11 or 13 components (

Table 1), but the stream may contain other components such as helium or hydrogen. The un-measured components in “pipeline quality” natural gas applications are typically less than 0.5% of the total concentration and do not significantly affect the calculation of the energy value. A second reason for the components not adding up to 100% is the change in atmospheric pressure causing the amount of sample injected into the columns to change. To inject a sample into the columns, a *sample loop* that has a fixed volume is purged with the sample gas. The sample injection valve then switches the flow path to push a fixed volume of sample into the chromatograph columns. However, the amount of sample injected is dependent on the pressure of the sample as the number of molecules in a fixed volume increases with pressure. To remove the sensitivity of the GC to variations in sample pressure from one stream to another, the sample loop is equalized to atmospheric pressure before the sample is injected into the columns. As the atmospheric pressure does change, the amount of sample injected will also change from one analysis to another.

Table 1 - The measurement ranges for the common GC applications for Natural Gas energy measurement

	C6+	C9+
Nitrogen	0 to 20	0 to 20
Carbon Dioxide	0 to 10	0 to 10
Methane	65 to 100	65 to 100
Ethane	0 to 20	0 to 20
Propane	0 to 10	0 to 10
n-Butane	0 to 5	0 to 5
i-Butane	0 to 5	0 to 5
neo-Pentane	0 to 1	0 to 1
iso-Pentane	0 to 1	0 to 1
n-Pentane	0 to 1	0 to 1
C6+	0 to 0.7	
Hexanes		0 to 1
Heptanes		0 to 1
Octanes		0 to 0.5
C9+		0 to 0.5

The calculations for the physical properties (such as BTU, specific gravity, and compressibility) assume that the composition will add up to 100%. To make the composition add up to 100%, the GC controller will *normalize* the results by mathematically adjusting every component by the same proportion to equal 100% (Table 2). The sum of the components before they are normalized is referred to as the *un-normalized total* and is used as a diagnostic for GC performance. Most operators use an alarm limit of +/- 2% from 100% (98% to 102%) for the un-normalized total. As the un-normalized total is the sum of the components as measured, it is an indicator of how much sample has been injected compared to the amount of sample injected during the calibration cycle. The formula for calculating the normalized concentration for each component is:

$$CONCN_n = \frac{CONC_n}{\sum_{k=1}^k CONC_k} \times 100 \quad (1)$$

where

$CONCN_n$ = Normalized concentration of component "n" in percent of total gas concentration

$CONC_n$ = Non-normalized concentration of component "n" in mole percent

$CONC_k$ = Non-normalized concentration of component "n" in mole percent for each "k" component

k = Number of components to be included in the normalization

Table 2 - The results as measured and the normalized values.

	Un-Normalized	Normalized
Nitrogen	0.987	1.000
Carbon Dioxide	0.494	0.500
Methane	93.518	94.750
Ethane	1.974	2.000
Propane	0.740	0.750
i-Butane	0.296	0.300
n-Butane	0.296	0.300
i-Pentane	0.148	0.150
n-Pentane	0.148	0.150
C6+	0.099	0.100
SUM	98.7	100

Calculating the BTU

The *Gross Heating Value* formula, given in the GPA 2172-09 standard, is used to calculate the gross heating value per unit volume at base temperature and pressure (Gas Processors Association, 2009, p. 5). The heating value can be calculated assuming the gas is free of water ("gross dry heating value" or "higher heating value"), saturated with water ("gross saturated heating value"), or "as delivered" in which the moisture content is measured and used in the calculations. In most pipeline applications, the gas is assumed to be "dry" (less than 7 lbs/scf of water) and the gross heating value is calculated.

$$Hv^{id}(\text{dry}) = \sum_{i=1}^N x_i Hv_i^{id} \quad (2)$$

where

Hv^{id} = gross heating value per unit volume at base pressure and temperature

x_i = the mole fraction of component i

N = the total number of components

Hv_i^{id} = the ideal heating value of component i

The ideal heating value for each component is provided in the GPA 2145-09 standard (Gas Processors Association, 2009). However, the values in the GPA 2145-09 tables are at a base pressure of 14.696 PSIA. The most common base pressure used in the United States is 14.73 PSIA, so the ideal heating values for each component are converted from the base pressure used in GPA 2145-09 to the base pressure used in the custody transfer agreement using the formula (Gas Processors Association, 2009, equation A.6)

$$Hv^{id} = Hv_{i(GPA2145)}^{id} \times \frac{P}{14.696} \quad (3)$$

where

P = Contract Base Pressure

The most common GC's used in custody transfer of natural gas is known as the C6+. This application measures nitrogen, carbon-dioxide, and each of the alkane hydrocarbons (molecules made up of hydrogen and carbon molecules with single bonds only) up to normal-pentane. Molecules larger than normal-Pentane are measured as a combined component peak, referred to as C6+. For the purposes of calculating the heating value and other physical properties, the composition of the C6+ fraction is assumed a fixed ratio. The ratios, often referred to as the C6+ *split*, commonly used in the United States is shown in Table 3.

Table 3 - Common assumed fractions for the C6+ component.

	C6+ Split Compositions			
	47/35/17	50/50/0	GPA2261	58/28/14
C6	47.466%	50.000%	60.000%	57.143%
C7	35.340%	50.000%	30.000%	28.572%
C8	17.194%	0.000%	10.000%	14.285%
$Hv^{id}(14.696)$	5276.5	5129.3	5129.1	5182.5
$Hv^{id}(14.73)$	5288.7	5141.1	5141.1	5194.5

While the process of calculating the heating value is done automatically by the GC controller, the calculation can be easily hand calculated like the example in Table 4. In this example, the heating value is calculated at the base pressure of 14.73 PSIA. The first step is to convert the heating values from GPA 2145-09 to the base pressure of 14.73 PSIA using equation (3), as is shown column 4. The amount of energy contributed by each component is calculated in column 5, and the sum of these values is the BTU value for that gas, at the defined standard pressure. For comparison, the BTU value is calculated at 14.696 PSIA in column 6 and the BTU value is over two

BTU/scf less than the value at 14.73 PSIA, highlighting the importance of using the correct reference pressures whenever performing custody transfer calculations.

An example of the difference between the different splits (and using only the n-Hexane heating value) is shown in Table 5.

Table 4 - Calculation of the heating value for a typical "pipeline" quality natural gas

1	2	3	4	5	6
	Mole %	H_v^{jd} GPA 2145-09	H_v^{jd} 14.73 PSIA	BTU/scf (14.73 PSIA)	BTU/scf (14.696 PSIA)
Nitrogen	1.000	0.0	0.0	0.00	0.00
Carbon Dioxide	0.500	0.0	0.0	0.00	0.00
Methane	94.750	1010.0	1012.3	959.19	956.98
Ethane	2.000	1769.7	1773.8	35.48	35.39
Propane	0.750	2516.1	2521.9	18.91	18.87
i-Butane	0.300	3251.9	3259.4	9.78	9.76
n-Butane	0.300	3262.3	3269.8	9.81	9.79
i-Pentane	0.150	4000.9	4010.2	6.02	6.00
n-Pentane	0.150	4008.7	4018.0	6.03	6.01
C6+ 47/35/17	0.100	5276.5	5288.7	5.29	5.28
BTU/scf				1050.50	1048.07

Table 5 - A comparison of the energy content calculated with different C6+ splits at 14.73 PSIA

		Heating Value Calculations with the various C6+ Ratios				
	Mole %	No Split	47/35/17	50/50/0	GPA2261	58/28/14
Nitrogen	1.000	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide	0.500	0.00	0.00	0.00	0.00	0.00
Methane	94.750	959.19	959.19	959.19	959.19	959.19
Ethane	2.000	35.48	35.48	35.48	35.48	35.48
Propane	0.750	18.91	18.91	18.91	18.91	18.91
i-Butane	0.300	9.78	9.78	9.78	9.78	9.78
n-Butane	0.300	9.81	9.81	9.81	9.81	9.81
i-Pentane	0.150	6.02	6.02	6.02	6.02	6.02
n-Pentane	0.150	6.03	6.03	6.03	6.03	6.03
C6+	0.100	4.77	5.29	5.14	5.14	5.19
BTU/scf		1049.98	1050.50	1050.35	1050.35	1050.40

Conclusion

The GC is the most common method of determining the energy content of natural gas for custody transfer. Ensuring the GC receives a sample that is representative of the gas going through the metering station is the first step in calculating the correct value. Once the GC has measured the composition, the controller normalizes the results for use in the fiscal calculations. Understanding the effect of the calculation base pressure and the selection of the fixed ratios used in the C6+ split will ensure that the energy values calculated are representative of the gas in the metering run and compatible with the other calculations in the fiscal transfer.

References:

Gas Processors Association. (2009). *GPA Standard 2145-09: Table of Physical Properties for Hydrocarbons and Other Compounds of Interest to the Natural Gas Industry*. Tulsa, OK: Gas Processors Association.

Gas Processors Association. (2009). *GPA Standard 2172-09: Calculation of Gross Heating Value, Relative Density, Compressibility and Theoretical Hydrocarbon Liquid Content for Natural Gas Mixtures for Custody Transfer*. Tulsa, OK: Gas Processors Association.