

HEAT QUANTITY CALCULATION RELATING TO WATER VAPOR IN NATURAL GAS

Class 5190

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Introduction

Natural gas oftentimes contains some amount of water, in either vapor or liquid form. The solubility of water in natural gas flowing through a pipeline is a function of the pressure and temperature of the flow stream. The amount of water affects the heating (calorific) value per unit volume of natural gas. The more water present in the gas, the less valuable it is as a fuel, since the water does not burn. This water, in vapor form, is sometimes referred to as “spectator” water and it displaces the hydrocarbon components in a natural gas mixture. The net effect is a reduction in heating value and monetary value per unit volume of gas. The amount of water vapor contained in a natural gas mixture is customarily expressed in terms of the mass of water per unit volume of gas; for example, pounds mass of water per million standard cubic feet of natural gas (lb_m/MMSCF).

If water is present in natural gas that is to be transported, a decision must be made as to whether or not the water should be removed. There is obviously a cost associated with removing and disposing of water extracted from natural gas. Even if the water is left in the gas to avoid the removal costs, there is still a cost, because the water has mass, which requires energy (or compression horsepower) to transport. Another important consideration is that water is one of the constituents that can cause corrosion in the steel pipes used to transport natural gas. Repairing or replacing corroded pipelines can be a significant expense. In addition, corroded pipelines may degrade operational safety and system reliability. There are also issues associated with how water adversely affects the combustion process when natural gas is used as a fuel. As one can see, there are a number of considerations to take into account when deciding how much water to remove from a natural gas flow stream. Gas transportation and delivery contracts and tariffs usually limit the amount of water allowed in transmission- and distribution-grade natural gas streams as one way to help control the amount of water introduced into the natural gas pipeline grid in the United States.

This paper explains how to account for water vapor when calculating the heating (or calorific) value of natural gas.

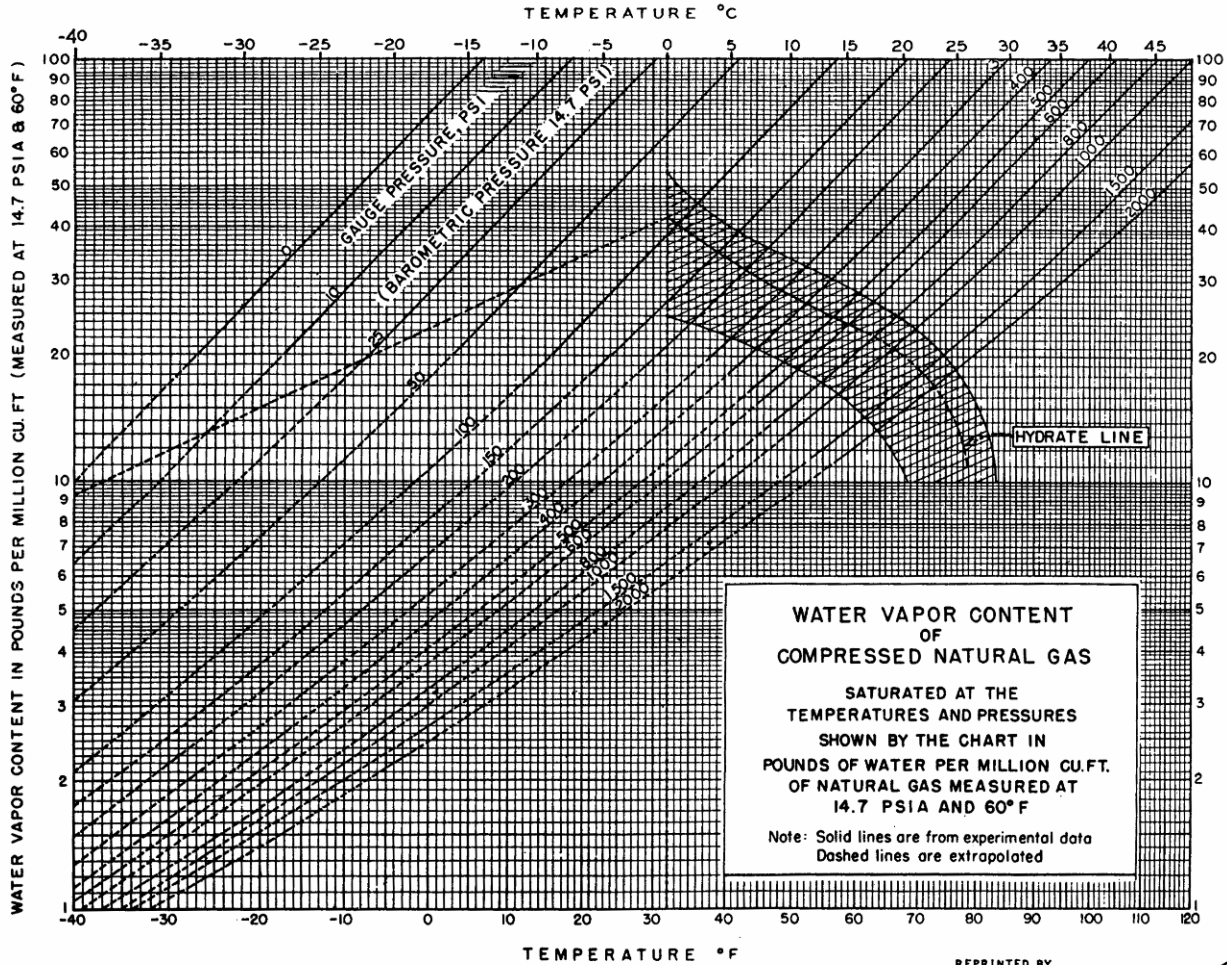
How much water can natural gas hold?

Natural gas can only hold a limited amount of water (in vapor form) in solution before the mixture reaches what is known as the saturation point. Natural gas should be referred to as “water-saturated” if, at an equilibrium condition, the amount of water in the gas equals the amount of water that the gas can hold without condensation occurring at a given temperature and pressure. Figure 1 shows the water solubility of typical transmission- or distribution-grade natural gas in terms of mass of water per unit volume (lb_m/MMSCF) of natural gas at “standard” conditions. The definition of “standard” conditions (sometimes also referred to as “base” conditions) can vary a bit, depending on the source of the information, but is usually defined as being at a temperature of about 60°F and a pressure of about 14.7 psia. Table 1 shows the mass-to-volume ratios for water vapor in compressed natural gas. Technically, a two-phase stream flowing natural gas and water is also water-saturated. However, two-phase streams are not considered for purposes of this discussion.

Water Dew Point for Natural Gas

When the amount of water in a natural gas mixture reaches the saturation point, the water is said to be at its dew point. The water dew point is typically different from the hydrocarbon dew point of a natural gas mixture. The water dew point is the condition (i.e., temperature and pressure) at which water in the mixture will begin to change phase (from vapor to liquid or vice versa), while the hydrocarbon dew point is the condition at which hydrocarbons in the mixture will begin to change phase. Figure 2 illustrates this difference. In this figure, the hydrocarbon dew point line is shown for a particular natural gas mixture, as are the water dew point lines for two different water concentration levels, that is, 7 and 80 lb_m/MMSCF .

Described another way, a water-saturated natural gas is a mixture at its water dew point.



FROM MONOGRAPH 8. "GAS HYDRATES AND THEIR RELATION TO THE OPERATION OF NATURAL GAS PIPE LINES." BY DEATON AND FROST. PUBLISHED JOINTLY BY U. S. BUREAU OF MINES AND THE AMERICAN GAS ASSOCIATION.

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Figure 1. Equilibrium Water Vapor Content of Compressed Natural Gas

lb _m /MMSCF	Volume %
5	0.0105
7	0.0147
10	0.021
20	0.042
30	0.063
40	0.084
50	0.105
60	0.126
70	0.147
80	0.168
90	0.189
100	0.21

Table 1. Mass-to-Volume Ratios for Water Vapor in Compressed Natural Gas

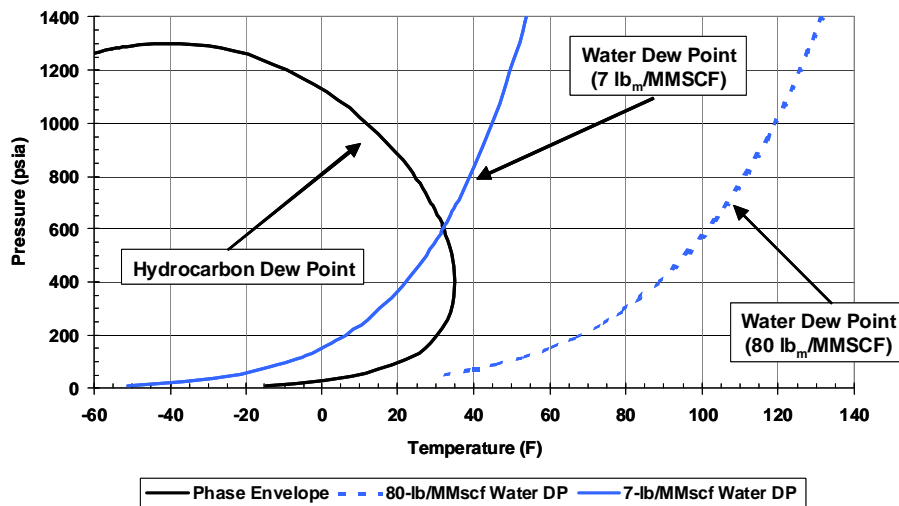


Figure 2. Example Hydrocarbon and Water Dew Points for a Natural Gas Mixture

Measuring Water Vapor in Natural Gas

There are several ways to determine experimentally the amount of water in a natural gas mixture. Following is a list of some of the measurement devices that are available. More detailed information on at least some of these devices can be found elsewhere in these Proceedings.

- Length-of-stain tubes: These are relatively inaccurate devices (e.g., one manufacturer reports a $\pm 25\%$ measurement uncertainty). Some use this device merely as a check, but not for accurate quantification.
- Dew scope (a.k.a., chilled mirror device or Bureau of Mines device): This method is an optical detection of water vapor condensation on a chilled mirror surface.
- Electrolytic sensors: This device adsorbs water vapor on a phosphorous pentoxide sensor.
- Capacitance sensors: With this device, a dielectric material absorbs moisture.
- Vibrating crystal sensors: The frequency of vibration of this device changes as moisture is absorbed by the sensing crystal.
- Laser-based sensors: Moisture absorbs laser light tuned to a specific wavelength.

Water Vapor Determination Standards

If it is not possible to directly measure the amount of water in a natural gas mixture using one of the methods described above, it is possible to estimate the amount using measured parameters associated with a particular natural gas mixture. These methods can also be used to estimate water dew point, given the water concentration at the saturation condition. Three of the more commonly used methods for determining water concentration are described in (1) the U.S. Bureau of Mines/American Gas Association (AGA) Monograph 8, (2) the Institute of Gas Technology (IGT) Research Bulletin No 8, and (3) the Gas Processors Suppliers Association (GSPA) Engineering Data Book. The Bureau of Mines/AGA Monograph 8 is entitled *Gas Hydrates and Their Relation to the Operation of Natural Gas Pipe Lines* (written by Deaton and Frost). The ITG Bulletin is entitled *Equilibrium Moisture Content of Natural Gases* (written by Bukacek) and includes a correlation developed using experimental measurements of methane, methane-ethane mixtures, and natural gas mixtures. This correlation is also referenced in American Society for Testing and Materials (ASTM) D1142-95(2006) entitled *Standard Test Method for Water Vapor Content of Gaseous Fuels by Measurement of Dew Point Temperature*. The GSPA Engineering Data Book includes a correlation plot published by McKetta and Wehe in 1958 and corrections for relative density (the corrections become more important for high relative densities).

Table 2 shows how these three methods compare in predicting water saturation concentration, given a measured dew point temperature of 30°F and a pressure of 1,000 psia. Figure 3 illustrates how these three methods compare in predicting dew point, given a water saturation concentration of 7 lb_m/MMSCF.

Method	lb _m /MMSCF
IGT 8	6.4
GPSA	6.2
AGA	7.5

Table 2. Predicted Water Content for a Dew Point Temperature of 30°F at a Pressure of 1,000 psia

Differences in Water Dew Points for 7 lb_m / MMSCFD Water Content

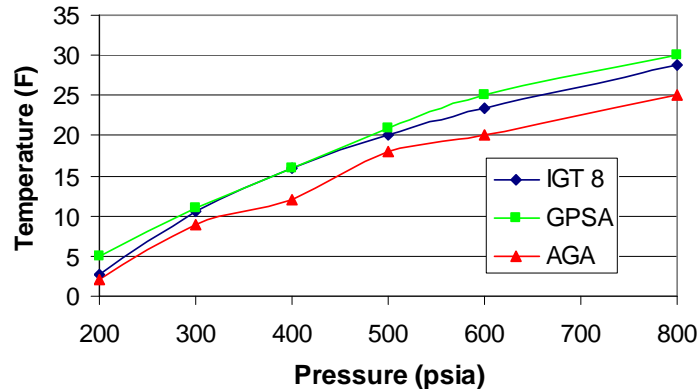


Figure 3. Comparison of Water Dew Points Predictions Using Various Correlations

The interested reader is referred to the preceding references for details about each predictive method for water dew point and concentration. For illustrative purposes, following is a description of the method found in IGT Research Bulletin No. 8 and ASTM D1142-95(2006). With this method, the water vapor concentration, W , can be calculated using the following equation (i.e., a modified form of Raoult's law):

$$W = (A / P_t) + B \quad \text{Equation 1}$$

where:

- W = water vapor concentration (lb_m/MMSCF)
- P_t = total pressure (psia)
- A = a constant proportional to the vapor pressure of water (see Table 3)
- B = a constant depending on temperature and gas composition (see Table 3)
(Values for B were computed from available data on methane, methane-ethane mixtures, and natural gases.)

(Raoult's law states that the vapor pressure of an ideal solution is dependent on the vapor pressure of each chemical component and the mole fraction of the component present in the solution.)

When using a predictive method, such as the one shown above, it is very important to know the range of applicability of the method and to stay within those limits when using the correlation. For example, ASTM D1142-95(2006) states that Equation 1 is believed to be accurate enough for the gaseous fuels industry, except for unusual situations where the dew point is measured at conditions close to the critical temperature of the gas.

Higher (Gross) Heating Value and Lower (Net) Heating value

Two key terms associated with natural gas containing some amount of water are "Higher (Gross) Heating Value" and "Lower (Net) Heating Value." Several, slightly different definitions exist for these two terms. Perhaps the most commonly referenced definition for Lower Heating Value (LHV) states that in reference to a combustion process in which natural gas is the fuel, the LHV is the enthalpy of all combustion products, minus the enthalpy of the fuel at the reference temperature, minus the enthalpy of the stoichiometric oxygen (O_2) at the reference temp-

Temperature (°F)	A	B	Temperature (°F)	A	B	Temperature (°F)	A	B
-40	131	0.22	70	17,200	7.17	180	357,000	74.8
-38	147	0.24	72	18,500	7.85	182	372,000	77.2
-36	165	0.26	74	19,700	8.25	184	390,000	79.9
-34	184	0.28	76	21,100	8.67	186	407,000	82.7
-32	206	0.30	78	22,500	9.11	188	425,000	85.8
-30	230	0.33	80	24,100	9.57	190	443,000	88.4
-28	256	0.36	82	25,700	10.0	192	463,000	91.4
-26	285	0.39	84	27,400	10.5	194	483,000	94.8
-24	317	0.42	86	29,200	11.1	196	504,000	97.7
-22	352	0.45	88	31,100	11.6	198	525,000	101
-20	390	0.48	90	33,200	12.2	200	547,000	104
-18	434	0.52	92	35,300	12.7	202	570,000	108
-16	479	0.56	94	37,500	13.3	204	594,000	111
-14	530	0.60	96	39,900	14.0	206	619,000	115
-12	586	0.64	98	42,400	14.6	208	644,000	119
-10	648	0.69	100	45,100	15.3	210	671,000	122
-8	714	0.74	102	47,900	16.0	212	698,000	126
-6	786	0.79	104	50,800	16.7	214	725,000	130
-4	866	0.85	106	53,900	17.5	216	754,000	134
-2	950	0.91	108	57,100	18.3	218	785,000	139
0	1,050	0.97	110	60,500	19.1	220	816,000	143
2	1,150	1.04	112	64,100	20.0	222	848,000	148
4	1,260	1.11	114	67,900	20.9	224	881,000	152
6	1,380	1.19	116	71,800	21.8	226	915,000	157
8	1,510	1.27	118	76,000	22.7	228	950,000	162
10	1,650	1.35	120	80,400	23.7	230	987,000	188
12	1,810	1.44	122	84,900	24.7	232	1,020,000	171
14	1,970	1.54	124	89,700	25.8	234	1,060,000	177
16	2,150	1.64	126	94,700	26.9	236	1,100,000	182
18	2,350	1.74	128	100,000	28.0	238	1,140,000	187
20	2,560	1.85	130	108,000	29.1	240	1,190,000	192
22	2,780	1.97	132	111,000	30.3	242	1,230,000	198
24	3,030	2.09	134	117,000	31.6	244	1,270,000	204
26	3,290	2.22	136	124,000	32.9	246	1,320,000	210
28	3,570	2.36	138	130,000	34.2	248	1,370,000	216
30	3,880	2.50	140	137,000	35.6	250	1,420,000	222
32	4,210	2.65	142	144,000	37.0	252	1,470,000	229
34	4,560	2.81	144	152,000	38.5	254	1,520,000	235
36	4,940	2.98	146	160,000	40.0	256	1,570,000	242
38	5,350	3.16	148	168,000	41.6	258	1,630,000	248
40	5,780	3.34	150	177,000	43.2	260	1,680,000	255
42	6,240	3.54	152	186,000	44.9	280	2,340,000	333
44	6,740	3.74	154	195,000	46.6	300	3,180,000	430
46	7,280	3.96	156	205,000	48.4	320	4,260,000	548
48	7,850	4.18	158	215,000	50.2	340	5 610 000	692
50	8,460	4.42	160	225,000	52.1	360	7,270,000	869
52	9,110	4.66	162	236,000	54.1	380	9,300,000	1,090
54	9,800	4.92	164	248,000	56.1	400	11,700,000	1,360
56	10,500	5.19	166	259,000	58.2	420	14,700,000	1,700
58	11,300	5.48	168	272,000	60.3	440	18,100,000	2,130
60	12,200	5.77	170	285,000	62.5	460	22,200,000	2,550
62	13,100	6.08	172	298,000	64.8			
64	14,000	6.41	174	312,000	67.1			
66	15,000	6.74	176	326,000	69.5			
68	16,100	7.10	178	341,000	72.0			

Note: To correct A and B to other base conditions, multiply each by: $(P_b/14.7) \times [519.6/(t_b + 459.6)] \times (0.998/Z_b)$

where:

- P_b = absolute base pressure (psia)
- t_b = base temperature (°F)
- Z_b = compressibility factor under base conditions

Table 3. Values of Constants A and B for Equation 1
 (Base conditions = 14.7 psia and 60°F)
 (Table excerpted from ASTM D1142-95(2006))

erature, minus the heat of vaporization of the vapor content of the combustion products. This definition is used by the Gas Processor Suppliers Association (GPSA) and, originally, by the American Petroleum Institute (API) for data collected for API Research Project 44. This definition for Lower Heating Value assumes that the latent heat of vaporization of water in the fuel and the reaction products are not recovered. Thus, the Lower Heating Value neglects the energy in the water vapor formed by the combustion of hydrogen in the fuel. This water vapor typically represents about 10% of the energy content. The Higher Heating Value (HHV) does not neglect the energy in the water vapor formed by the combustion of hydrogen in the fuel. The natural gas industry in the United States prefers to express the heating value of natural gas as the Higher (Gross) Heating Value.

$$HHV - LHV = H_w(id) - H_w(l)$$

Equation 2

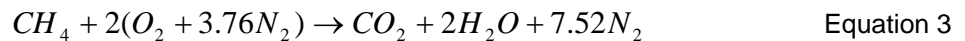
where:

- HHV = Higher (Gross) Heating Value
- LHV = Lower (Net) Heating Value
- $H_w(id)$ = Enthalpy of water vapor at ideal conditions
- $H_w(l)$ = Enthalpy of liquid water

The quantity $[H_w(id) - H_w(l)]$ is the ideal enthalpy of vaporization.

Stoichiometric (Ideal) Combustion

Stoichiometric combustion occurs when a fuel is burned *completely* with the minimum amount of air required for the fuel to burn. When calculating a stoichiometric combustion process, it is assumed that both the fuel and the air (oxidizer) are “dry” - free of any water, in either vapor or liquid form. It is also assumed that there is no sulphur in the fuel. To illustrate the concept, following is the equation for the stoichiometric combustion of pure methane:



Equation 3

where:

- CH_4 = methane
- O_2 = oxygen
- N_2 = nitrogen
- CO_2 = carbon dioxide
- H_2O = water

The resulting products of the *complete* combustion of *pure* methane are carbon dioxide, water, and nitrogen (). Because impurities typically exist in the fuel, the actual combustion products will likely include carbon (C), hydrogen (H_2), carbon monoxide (CO), hydroxide (OH), nitrogen oxide (NO_x), and sulphur oxide (SO_x), in addition to the carbon dioxide, water, and nitrogen. Figure 4 illustrates the basic combustion process. The parameter h_{fg} represents the latent heat (or enthalpy) of vaporization of water, which is the amount of energy required to change water from liquid to vapor without a change in temperature.

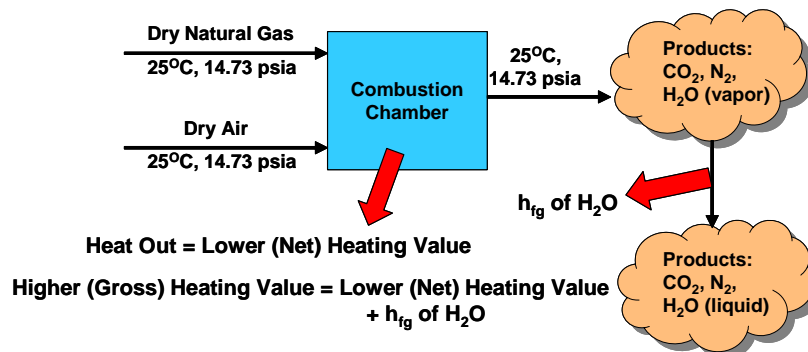


Figure adapted from *Thermodynamics – An Engineering Approach*, by Y.A. Cengel and M.A. Boles, McGraw-Hill, 1989

Figure 4. Illustration of the Combustion Process

Enthalpic differences due to different thermodynamic states of the fuel, air, and by-products can also affect the heating value of the natural gas. This effect is usually difficult to compute and oftentimes considered negligible (i.e., ~0.005%). The compressibility of the gas (i.e., the adjustment of heating value from an “ideal” to a “real” gas state) can also affect the heating value determination, as can the presence of water vapor.

Adjusting Natural Gas Energy Content for the Effect of Water

When determining energy flow rate or the amount of energy delivered over a period with a natural gas stream, one can adjust either the volumetric flow rate (or the total volume delivered) or the heating value per unit volume

of the natural gas to account for any water present in the gas stream. Note, however, that one should not adjust both the volumetric flow rate and the heating value of the gas.

By adjusting the volume to account for water (vapor), one effectively removes the water from the gas stream, leaving only the hydrocarbons and any diluents, such as carbon dioxide, nitrogen, or other trace components. In many instances, the compositional makeup of a natural gas mixture is determined from an analysis from a gas chromatograph (GC), in which case there is no need to adjust the gas composition to account for water vapor because a GC does not typically measure the amount of water, if any, in a gas sample. If, instead, one adjusts the heating value to account for water (vapor), one is essentially including water as a component of the natural gas mixture. In that case, there is no need to adjust the measured volume, because the measurement includes the water vapor. With either approach, the energy flow rate (or total amount of energy delivered) decreases due to the presence of the water.

When accounting for water and its effect on the heating (calorific) value of a natural gas mixture, the heating value per unit volume of gas can be reported several ways: (1) on a “dry” gas basis, (2) on a saturated gas basis at “standard” (or “base,” if different than “standard”) conditions, or (3) on an actual flowing conditions basis.

The volume fraction of water vapor in a natural gas mixture can be expressed as follows:

$$X_{H_2O} = P_w / P_t \quad \text{Equation 4}$$

where:

- X_{H_2O} = volume fraction of water vapor
- P_w = partial pressure of water vapor
- P_t = total pressure of the natural gas mixture

The heating value of “dry” gas is related to the volume fraction of water vapor in a natural gas mixture as shown in the following equation:

$$H_{v,dry} = H_{v,saturated} (1 - X_{H_2O,saturated}) \quad \text{Equation 5}$$

where:

- $H_{v,dry}$ = heating value of “dry” natural gas
- $H_{v,saturated}$ = heating value of water-saturated natural gas
- $X_{H_2O,saturated}$ = volume fraction of water vapor at water-saturated conditions

The quantity $(1 - X_{H_2O,saturated})$ is sometimes referred to as the “moisture factor.”

Example Calculations

Assume a natural gas mixture is flowing through a transmission pipeline at a pressure of 500 psia and that the (measured) water dew point temperature is 70°F. Also, assume that a gas chromatograph is used to obtain a compositional analysis of the gas mixture and that the resulting “dry” heating value, $H_{v,dry}$, obtained from the GC analysis is found to be 1,025 BTU/SCF (i.e., at 14.7 psia and 60°F). (Remember, a GC analysis typically does not account for any water vapor in the mixture).

Using Table 1 in ASTM D1142-95(2006) as a reference (i.e., Table 4 that follows), the saturation vapor pressure of water at 70°F is determined to be 0.36326 psia. Using Equation 4, the calculated value for the volume fraction of the water vapor, X_{H_2O} , would then be 0.000727 or about 0.073% of the total volume of the gas mixture. Using Equation 5, the calculated heating value of water-saturated natural gas at this condition, $H_{v,saturated}$, would be 1,024.3 BTU/SCF, meaning the water vapor reduces the heating value of the natural gas mixture by about 0.073%.

Conclusions

As explained above, the amount of water in natural gas affects the heating (calorific) value per unit volume. The more water present in the gas, the less valuable it is as a fuel, since the water does not burn. There is a cost associated with removing water from natural gas. There are also operational, environmental, and economic issues associated with leaving the water in the natural gas. It is important to know precisely how much water is

contained in a natural gas mixture so that a proper assessment can be made regarding whether or not to remove the water. As outlined herein, there are a number of methods available to help characterize the amount of water contained in any given natural gas mixture. When determining energy flow rate or the amount of energy delivered over a period with a natural gas stream, one can adjust either the volumetric flow rate (or the total volume delivered) or the heating value per unit volume of the natural gas to account for any water present in the gas stream. Note, however, that one should not adjust both the volumetric flow rate and the heating value of the gas. The interested reader is referred to the various industry standards and technical reports referenced herein for more details about quantifying the amount of water in a natural gas mixture.

Temperature (°F)	Vapor Pressure of Liquid Water (mm Hg)	Vapor Pressure of Liquid Water (psia)	Vapor Pressure of Ice (mm Hg)	Vapor Pressure of Ice (psia)	Specific Volume of Saturated Water Vapor (ft ³ /lb _m)	Temperature (°F)	Vapor Pressure of Liquid Water (psia)	Specific Volume of Saturated Water Vapor (ft ³ /lb _m)
0	1.139	0.02202	0.958	0.01852	14810			
1	1.195	0.02311	1.010	0.01953	14080	51	0.18485	1644.2
2	1.251	0.02419	1.063	0.02056	13400	52	0.19182	1587.6
3	1.310	0.02533	1.120	0.02166	12750	53	0.19901	1533.2
4	1.373	0.02655	1.180	0.02282	12140	54	0.20644	1480.9
5	1.436	0.02777	1.241	0.02400	11550	55	0.21411	1430.6
6	1.505	0.02910	1.308	0.02529	11000	56	0.22203	1382.2
7	1.573	0.03042	1.374	0.02657	10480	57	0.23021	1335.6
8	1.647	0.03185	1.446	0.02796	9979	58	0.23865	1290.9
9	1.723	0.03332	1.521	0.02941	9507	59	0.24736	1247.8
10	1.807	0.03494	1.599	0.03092	9060	60	0.25635	1206.3
11	1.883	0.03641	1.681	0.03251	8636	61	0.26562	1166.4
12	1.970	0.03809	1.767	0.03417	8234	62	0.27519	1128.0
13	2.057	0.03978	1.856	0.03589	7851	63	0.28506	1091.0
14	2.149	0.04156	1.950	0.03771	7489	64	0.29524	1055.4
15	2.247	0.04345	2.050	0.03964	7144	65	0.30573	1021.1
16	2.345	0.04535	2.151	0.04159	6817	66	0.31655	88.03
17	2.450	0.04737	2.260	0.04370	6505	67	0.32770	956.19
18	2.557	0.04944	2.373	0.04589	6210	68	0.33920	925.51
19	2.607	0.05163	2.489	0.04813	5929	69	0.35105	895.94
20	2.785	0.05385	2.610	0.05047	5662	70	0.36326	867.44
21	2.907	0.05621	2.740	0.05298	5408	71	0.37584	839.97
22	3.032	0.05863	2.872	0.05554	5166	72	0.38879	813.48
23	3.163	0.06116	3.013	0.05826	4936	73	0.40214	787.94
24	3.299	0.06379	3.160	0.06110	4717	74	0.41588	763.31
25	3.433	0.06638	3.310	0.06401	4509	75	0.43004	739.55
26	3.585	0.06932	3.471	0.06712	4311	76	0.44461	716.62
27	3.735	0.07222	3.636	0.07031	4122	77	0.45961	694.51
28	3.893	0.07528	3.810	0.07367	3943	78	0.47505	673.16
29	4.054	0.07839	3.989	0.07714	3771	79	0.49094	652.56
30	4.224	0.08168	4.178	0.08079	3608	80	0.50729	632.68
31	4.397	0.08502	4.373	0.08456	3453	81	0.52411	613.48
32	4.579	0.08866	4.579	0.08854	3301.9	82	0.54142	594.95
33		0.09230			3178.0	83	0.55922	577.05
34		0.09607			3059.2	84	0.57753	559.76
35		0.09998			2945.5	85	0.59636	543.07
36		0.10404			2836.4	86	0.61573	526.94
37		0.10823			2731.9	87	0.63563	511.35
38		0.11258			2631.7	88	0.65609	496.29
39		0.11708			2535.7	89	0.67713	481.73
40		0.12173			2443.5	90	0.69874	467.66
41		0.12655			2355.1	91	0.72095	454.06
42		0.13154			2270.3	92	0.74377	440.91
43		0.13670			2188.9	93	0.76722	428.19
44		0.14204			2110.8	94	0.79130	415.89
45		0.14756			2035.8	95	0.81604	403.99
46		0.15328			1963.8	96	0.84144	392.48
47		0.15918			1894.6	97	0.86753	381.35
48		0.16528			1828.2	98	0.89431	370.58
49		0.17159			1764.4	99	0.92180	360.15
50		0.17812			1703.1	100	0.95003	350.06

NOTE: The values for vapor pressure from 0 to 32°F were calculated from data in the International Critical Tables. All other values were taken from Harr, Gallagher, and Kell, "NBSINRC Steam Tables," National Standard Reference Data System, 1984, p. 9. Data on specific volumes of saturated water vapor from 0 to 32°F were obtained from J. A. Goff and S. Gratch, "Low-Pressure Properties of Water from -160 to 212°F," *Heating, Piping, and Air Conditioning*, Volume 18, No. 2, February 1946, pp. 125-136.

Table 4. Vapor Pressures and Specific Volumes of Saturated Water Vapor at Various Temperatures
(Table excerpted from ASTM D1142-95(2006))

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