

## The Natural Gas Composition is Key in Hydrate Formation

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### Abstract

This analysis will evaluate the effects of the natural gas composition on the formation of hydrate for the purpose of storage and transporting natural gas.

Results show that the composition of the natural gas can affect the temperature and pressure required for formation of the hydrate. Carbon dioxide, hydrogen sulfide and nitrogen impurities in natural gas affect the hydrate formation and may result in additional processing of the gas is required hydrate formation.

The composition of the sample also affects the water to gas mole ratio and hence the amount of water required for hydrate formation.

**Key words:** Gas; Composition; Hydrate formation

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### INTRODUCTION

Gas hydrate may be a viable means of capturing, storing and transporting stranded, flared and associated gas. The ability of natural gas to form hydrate in combination with water is a very interesting and useful concept which could be widely utilized in the industry.

The composition of the natural gas from the well is very important in the hydrate formation process as it

affects the gas hydrate value chain. Gas from the well is first expanded to achieve the condition required for hydrate formation. The composition of the gas affects the expansion process since the resulting fluid may be in single phase or two phases. For hydrate formation the gas must remain in the single phase after expansion otherwise additional gas processing is required.

The composition of the gas captured in hydrate form would determine the heating value of the natural gas transported. This is important since natural gas is sold to meet a heating value standard. The particular natural gas composition of the sample must be evaluated for the hydrate formation process because it may not meet heating value requirement, remain in the single gas phase after expansion and require additional separation for samples with large amounts of impurities.

Technological advancement in utilizing gas hydrate as means of transporting natural gas could be a key component in capturing stranded, associated gas and in some cases unconventional gas. There is still about 40% of natural gas stranded reserves to be monetized (Fleisch, 2006).

The composition of gas is very important and such proper evaluation must be done to ensure the gas sample is adequate for transportation via gas hydrate. The natural gas must remain in the gaseous phase after expansion prior to hydrate formation. Most of the previous studies focused on simple gases such as methane and ethane. Most natural gas has much more components than just methane and ethane and hence the composition can have significant impact on hydrate formation. In this analysis, twenty one natural gas compositions of typical wells are analyzed to convert and transport 5 MMscf/d of gas in hydrate state to neighboring islands (e.g.). The natural gas streams obtained from these wells were, generally, sweet gases (without H<sub>2</sub>S) and ranges in composition from C<sub>1</sub> to C<sub>10</sub>. These samples are shown in Table 1.

**Table 1**  
**Natural Gas Composition from Trinidad/Mole %**

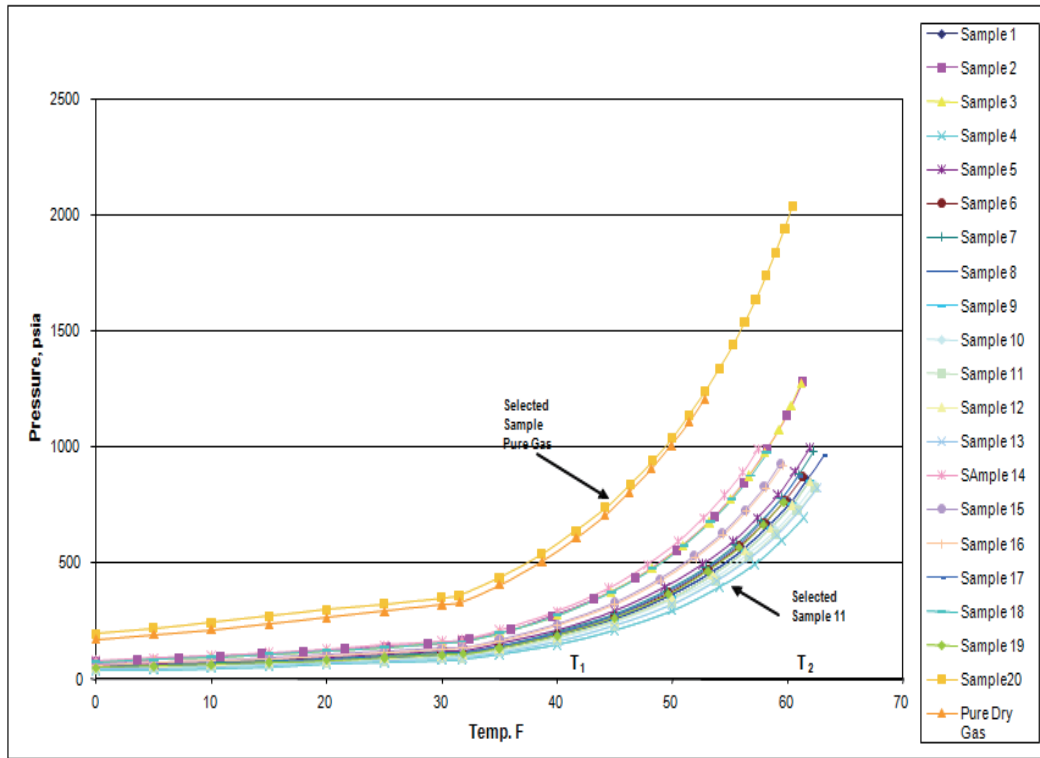
Sample		1	2	3	4	5	6	7	8	9	10
Nitrogen	N2	0.56	0.78	3.93	0.87	1.32	2.40	0.60	2.21	1.09	2.55
Hydrogen Sulphide	H2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide	CO2	3.92	2.84	2.98	3.75	0.90	0.64	4.64	1.12	1.73	0.44
Methane	C1	92.09	92.04	88.29	87.77	88.02	88.37	87.48	86.21	85.20	85.04
Ethane	C2	2.52	2.82	3.05	4.86	6.60	5.03	4.85	6.47	6.76	7.00
Propane	C3	0.51	0.74	0.65	1.51	1.63	1.77	1.91	2.32	2.73	3.23
Isobutane	iC4	0.10	0.14	0.24	0.31	0.20	0.65	0.34	0.44	0.36	0.32
N-Butane	nC4	0.12	0.21	0.30	0.41	0.55	0.49	0.54	0.65	1.00	0.82
Isopentane	iC5	0.05	0.10	0.14	0.19	0.17	0.20	0.21	0.25	0.30	0.16
N-Pentane	nC5	0.04	0.08	0.14	0.12	0.21	0.15	0.16	0.18	0.38	0.20
Hexanes plus	C6	0.04	0.08	0.14	0.12	0.21	0.15	0.16	0.18	0.38	0.20
Hexanes	C6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptanes	C7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Octanes	C8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Nonanes	C9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Decanes +	C10+	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Sample		11	12	13	14	15	16	17	18	19	20	Dry gas
Nitrogen	N2	0.46	1.09	0.49	0.06	0.09	0.09	0.09	0.21	0.00	0.05	0.00
Hydrogen Sulphide	H2S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Carbon Dioxide	CO2	6.11	1.73	5.84	0.10	0.31	0.58	0.68	0.94	0.37	0.02	0.00
Methane	C1	77.25	85.20	78.07	96.82	93.42	91.65	89.55	94.70	92.28	99.63	99.00
Ethane	C2	8.77	6.76	8.96	1.75	2.96	3.48	4.14	2.90	1.48	0.17	1.00
Propane	C3	3.35	2.73	3.34	0.64	1.15	1.31	1.83	0.74	2.23	0.03	0.00
Isobutane	iC4	0.75	0.36	0.71	0.18	0.34	0.30	0.63	0.15	0.70	0.01	0.00
N-Butane	nC4	1.32	1.00	1.21	0.19	0.33	0.39	0.93	0.17	0.91	0.02	0.00
Isopentane	iC5	0.44	0.30	0.35	0.08	0.15	0.16	0.53	0.06	0.79	0.01	0.00
N-Pentane	nC5	0.69	0.38	0.50	0.06	0.11	0.16	0.47	0.05	0.09	0.02	0.00
Hexanes plus	C6+	0.86	0.45	0.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hexanes	C6	0.00	0.00	0.00	0.05	0.16	0.22	0.53	0.04	0.37	0.02	0.00
Heptanes	C7	0.00	0.00	0.00	0.04	0.25	0.28	0.38	0.02	0.30	0.00	0.00
Octanes	C8	0.00	0.00	0.00	0.02	0.18	0.39	0.18	0.02	0.25	0.00	0.00
Nonanes	C9	0.00	0.00	0.00	0.01	0.16	0.23	0.05	0.00	0.13	0.00	0.00
Decanes +	C10	0.00	0.00	0.00	0.00	0.39	0.76	0.01	0.00	0.10	0.02	0.00

### Effect on Natural Gas Hydrate Forming Conditions

The hydrate forming temperature/pressure for the twenty one natural gas streams given in Table 1 is plotted in Figure 1. This graph was developed on the basis of a large

number of data points generated by computer using the PVTsim program (PVTsim, 18). Figure 1 shows that the hydrate forming temperature/pressure relationship for natural gases is greatly influenced by the composition of the gas mixtures.

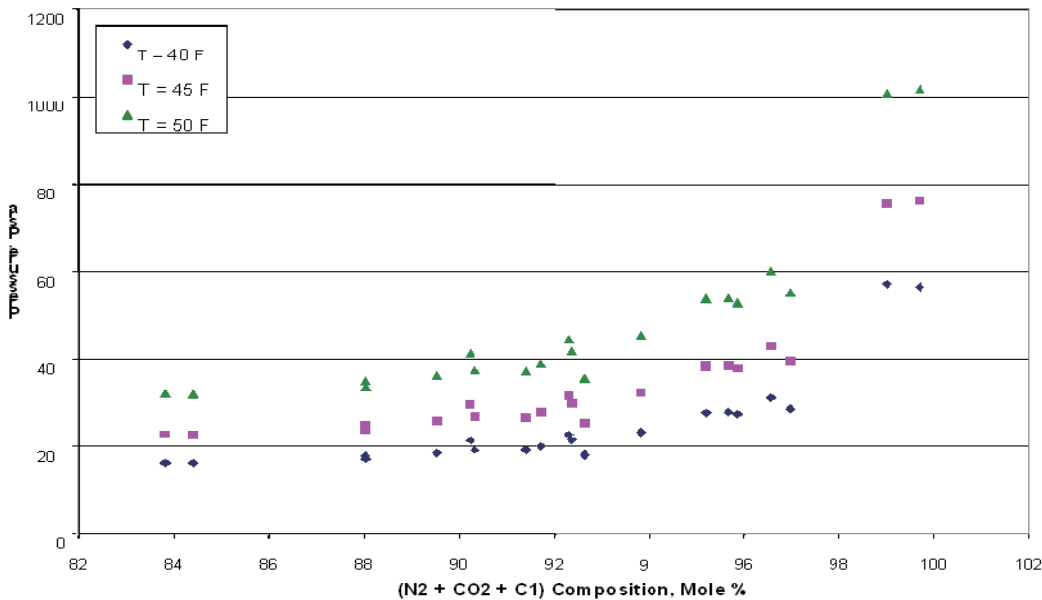


**Figure 1**  
 Hydrate forming temperature/pressure

The uppermost curve corresponds to the natural gas obtained from sample Dry Gas while the lowermost curve corresponds to the natural gas obtained from the Sample

11. At a fixed pressure, i.e. 600 psi sample 11 will form hydrates if the temperature is lower than  $T_2$ , while sample dry gas will form hydrate if  $T$  is lower than  $T_1$ .

**Effect of Composition on Hydrate Formation Pressure**



**Figure 2**  
 Hydrate formation pressure for different compositions (light components) from the 21 samples

Figure 2 shows the effect of the light components ( $N_2 + CO_2 + C_1$ ) on hydrate formation pressures at temperatures of 40 F, 45 F and 50 F. The points, in Fig. 2 correspond to the natural gas streams shown above. It is observed that as

the ( $N_2 + CO_2 + C_1$ ) composition varied from 84 mol% to 99 mol%, the hydrate formation pressure increases from 161.5 psi to 572.1 psi at 40 °F. Similar trends can be seen at the temperatures 45 F and 50 F.

The influence of the heavier is opposite to that observed in Figure 2 i.e., varying (C2 + C3 + iC4 + nC4 + iC5 + nC5 +C6+) concentration from 0.3 mol% to 16.2 mol%, the hydrate formation pressure decreases from 565.2 psi to 161.4 psi approximately, at 40 F.

## ESTIMATION OF MOLE RATIO MOLE REQUIRED FOR ALL SAMPLES

As indicated earlier, the formation conditions of 600 psia and 35 F were then chosen as it represents potential upscaling conditions deduced from experimental studies conducted by Okutani et al, 2007. The water to gas mole ratios for all samples was estimated for conditions of 600 psia and 35 F using the commercial simulator (PVTSim, 18). This was done by changing the mole ratio at this specific temperature and pressure until 100 % volume of hydrate is formed. The results are shown in Table 22 below. If excess water is used in the formation of the hydrate (e.g 7:1 mole ratio), a hydrate phase and aqueous phase is obtained.

**Table 2**  
**Actual Water to Gas Mole Ratio for all Samples (600 psia and 35 F)**

Sample	Mole ratio	Amount of water for 5MMscf/d, bbls
Sample 1	6.284	4249
Sample 2	6.264	4236
Sample 3	6.32	4274
Sample 4	6.23	4213
Sample 5	6.22	4206
Sample 6	6.26	4233
Sample 7	6.21	4199
Sample 8	6.25	4226
Sample 9	6.16	4166
Sample 10	6.24	4220
Sample 11	6.10	4125
Sample 12	6.16	4166
Sample 13	6.05	4091
Sample 14	6.28	4247
Sample 15	6.18	4179
Sample 16	6.10	4125
Sample 17	6.09	4118
Sample 18	6.29	4254
Sample 19	6.11	4132
Sample 20	6.31	4267
Sample Dry Gas	6.29	4254

The results show the range of mole ratio from 6.1:1 to 6.32:1 above the 6:1 mole. For 5 MMscf/d, this represent an additional 68–218 bbls of water required when

considering all samples. This is an additional 1.6–5.1% change in water needed. Commercial flow meters are capable of handling such this % change. It is important to note that while the mole ratios do not change substantially, the actual water needs will change greatly with the amount of MMscf/d of gas processed (Rajnauth et al, 2012). The amount of water required for a gas rate of 5 MMscf/d for sample with a mole ratio of 6.29:1 is evaluated as follows.

This was calculated as follows:

$$n_g = \frac{V_g P_{sc}}{RT_{sc}}$$

$$\frac{n_w}{n_g} = 6.29$$

$$n_w = \frac{\rho_w V_w}{MW_w}$$

$$V_w = \frac{6.29 n_g MW_w}{\rho_w}$$

where

$n_g$  moles of gas

$V_g$  volume of gas, 0.5 MMscf

$P_{sc}$  standard pressure, 14.71 psi

$R$  gas constant, 10.73 ft<sup>3</sup>psiR<sup>-1</sup>lbmol<sup>-1</sup>

$T$  standard temperature, 520 R

$n_w$  moles of water

$MW_w$  molecular weight water, 18

$\rho$  density of water, 62.48 lbm/ft<sup>3</sup>

$V_w$  volume of water, bbls

For 5MMscf/d

$$n_g = \frac{5000000 \times 14.71}{10.73 \times 520} = 13180$$

$$V_w = \frac{6.29 \times 13180 \times 18}{62.48 \times 5.615} = 4254 \text{ bbls}$$

For capturing 5MMscf of dry gas sample, 4250 bbls of water is required. The amount of water required for all samples are also shown in Table 2

## ESTIMATION OF HEATING VALUES OF GAS SAMPLES

The heating values of all samples were estimated:

- To use in energy balance calculations for entire process since it gives an indication of the amount of energy transported in the gas.

- To determine gas acceptance at markets around the world or whether further gas processing required. This is important since gas is sold based on its heating value.

The heating values were estimated simply by multiplying the ideal heating values of the individual component by the mole fraction which gives a simply approximation.

The computed heating value of the gas Sample 2 was 1029 Btu/scf before the hydrate formation, and 1014 Btu/scf after. This is because the hydrate formation separates the heavier components (> C5) as useful natural gas liquid. 0.02 MMscf (3829 bbls) of natural gas liquids are obtained with a heating value of 4441 Btu/scf while 4.98 MMscf natural gas (C<sub>1</sub> to C<sub>4</sub>) is stored in hydrate form. The heating values of the samples are shown in **Tables 3, 4 and 5** below. These include Sample 2 before and after hydrate formation, and the natural gas liquids separated during hydrate formation.

**Table 3**  
**Estimation of Heating Value of Sample 2 Before Hydrate Formation**

Sample 2 before hydrate formation		Mol %	Ideal heating value Btu/scf	Gas mix before hydrate Btu/scf
Nitrogen	N2	0.78	0.0	0.0
Carbon Dioxide	CO2	2.84	0.0	0.0
Methane	C1	92.04	1010.0	929.6
Ethane	C2	2.82	1769.7	49.9
Propane	C3	0.74	2516.1	18.6
Iso-butane	iC4	0.14	3251.9	4.6
N-Butane	nC4	0.21	3262.3	6.9
Iso-pentane	iC5	0.1	4000.9	4.0
N-Pentane	nC5	0.08	4008.9	3.2
Hexanes	C6	0.25	4755.9	11.9
Total		100		1029

**Table 4**  
**Estimation of Heating Value of Sample 2 After Hydrate Formation**

Sample 2 after hydrate formation		Mol %	Ideal heating value Btu/scf	Gas mix in hydrate Btu/scf
Nitrogen	N2	0.78	0.0	0.0
Carbon Dioxide	CO2	2.85	0.0	0.0
Methane	C1	92.44	1010.0	933.6
Ethane	C2	2.83	1769.7	50.1
Propane	C3	0.74	2516.1	18.7
Iso-butane	iC4	0.14	3251.9	4.6
N-Butane	nC4	0.21	3262.3	6.9
Total		100		1014

**Table 5**  
**Estimation of Heating Value of Natural Gas Liquids for Sample 2**

Natural gas liquids			Ideal heating value Btu/scf	NGL heating value Btu/scf
		Mol %		
Iso-pentane	iC5	23.3	4000.9	930.5
N-Pentane	nC5	18.6	4008.9	745.8
Hexanes	C6	58.1	4755.9	2765.1
Total		100.0		4441

The heating value estimates for all samples are shown in **Table 6**. The heating values before hydrate formation, the heating values of gas captured in hydrate form and the heating values of the natural gas liquids separate during the formation process are all highlighted in the table.

**Table 6**  
**Estimation of Heating Values Before and After Hydrate Formation and for Natural Gas Liquids for All Samples**

Sample	Heating value before hydrate btu/ft <sup>3</sup>	Heating value in hydrate btu/ft <sup>3</sup>	Heating value of NGL btu/ft <sup>3</sup>
Sample 1	1003	996	4380
Sample 2	1029	1014	4441
Sample 3	1004	985	4380
Sample 4	1056	1039	4308
Sample 5	1106	1080	4390
Sample 6	1091	1070	4351
Sample 7	1074	1053	4321
Sample 8	1103	1085	4199
Sample 9	1142	1106	4304
Sample 10	1127	1108	4306
Sample 11	1173	1109	4330
Sample 12	1142	1106	4304
Sample 13	1153	1109	4294
Sample 14	1056	1040	4667
Sample 15	1131	1062	6036
Sample 16	1181	1066	6272
Sample 17	1176	1098	4729
Sample 18	1045	1039	4557
Sample 19	1169	1089	5014
Sample 20	1015	1012	5288
Sample Dry Gas	1018	1018	0

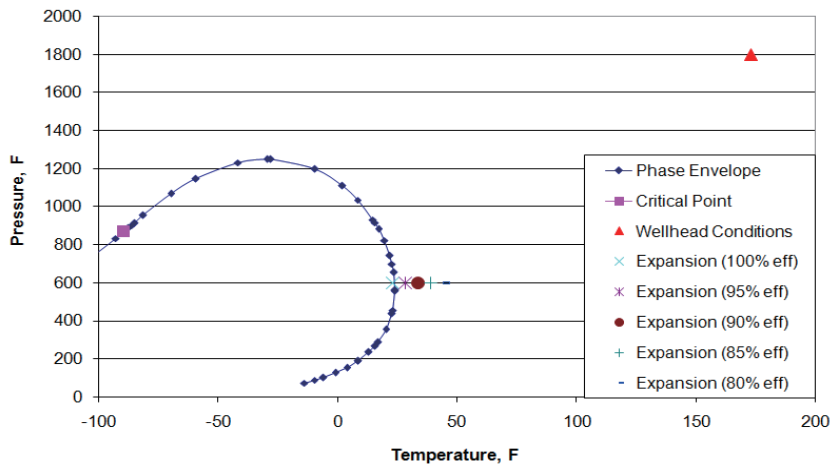
Gas may be transported to different regions around the world and therefore would be required to meet that region's heating value standard. The accepted heating value range accepted in the US is in the range 966–1120 Btu/scf. For Europe, the range is 940–1204 Btu/scf and for Japan 1065–1160 Btu/scf is required.

## EXPANSION OF GAS SAMPLES TO HYDRATE FORMATION CONDITIONS

The expansion process must also ensure the gas sample remains in the single-phase region of the phase diagram, which is important in the design process (Rajnauth et al, 2013). From the wellhead, the gas flows through a turbo-

expander, which causes the gas temperature to drop to 35 F, and the pressure to drop to 600 psia, assuming an efficiency of 85% or 90% depending on the sample.

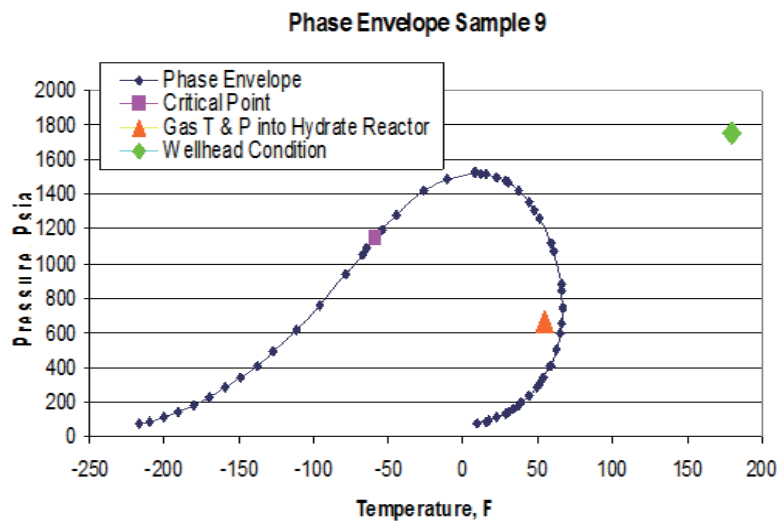
**Figure 1** shows the phase diagram for sample 2 with wellhead and outlet conditions, and with varying expansion efficiencies. Note that at 100% efficiency, the gas is very close to the two phase region.



**Figure 1**  
Phase diagram for sample 2

The expansion process for sample 2 remains in the single phase region of the phase diagram, which is important in the design process. However as seen in **Figure 4** the expansion process for sample 9 goes into the

two phase region of the phase diagram and therefore not suitable for natural gas hydrate formation unless further separation is carried out.



**Figure 4**  
Phase diagram for sample 2

## DISCUSSION

The composition of the sample must be evaluated for hydrate formation and transportation and should (a) Ensure heating value is within an acceptable range of 960-1120 Btu/scf. (b) Ascertain if the sample is appropriate for gas hydrate process since the sample must remain in the gaseous phase after expansion. If the sample goes into the

two-phase region after expansion additional separation is required and this was not analyzed in this study.

The exact amount of water for a particular volume of gas can be determined. The composition of the sample affects the mole ratio and hence the amount of water needed.

Higher components of the natural gas such as pentane and higher are not captured in the hydrate and separated out as natural gas liquids (NGLs). This can provide additional fuel for many processes.

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## CONCLUSIONS

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The composition of gas is very important and such proper evaluation must be done to ensure the gas sample is adequate for transportation via gas hydrate. The natural gas must remain in the gaseous phase after expansion prior to hydrate formation.

Impurities affect the hydrate PT equilibrium. Carbon dioxide increases the PT equilibrium line while nitrogen reduces it. At a fixed temperature, the higher the % methane in the sample the higher the hydrate formation pressure while the higher the propane levels the lower the formation pressure.

The mole ratio (hydrate number) is approximately 6; however, the actual hydrate number depends on the composition, temperature and pressure. It ranges from 6.1:1 to 6.32:1 for the samples evaluated.

The expansion process ensured that sample 2 remain in the single-phase region of the phase diagram, while Sample 9 goes into the two-phase region and therefore require additional separation before expansion. This is important in the design process.

- As shown in the analysis some natural gas sample:
- May not meet heating value requirement around the world
  - May not remain in the single gas phase after expansion
  - May require additional separation for samples with large amounts of impurities

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