EVALUATION OF CHARTS IN DETERMINING WATER CONTENT OF SWEET NATURAL GAS WITH METHANE COMPONENT OF 60 - 67%

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ABSTRACT

Published studies had shown that the majority of the charts for determining the water content of natural gases, were developed from gas compositions with methane component greater than 70%. Limited information exists on their ability to provide reliable and accurate results for gas compositions with a methane fraction below 70%. As a result, this study was on the validation of five (5) existing charts; commonly used in the natural gas industry; with the Cubic Plus Association Equation of State (CPA-EoS) and published experimental water content data, to ascertain their accuracy and reliability. The result of the study showed that all the charts, comprising the McKetta and Wehe, Campbell, Gordon, Katz, and the Guo and Ghalambor charts, gave relatively accurate results with average absolute deviations of less than 10%. When used with care, the McKetta and Wehe, Campbell, Gordon, Katz, and the Guo and Ghalambor charts, are recommended for use in estimating water content of sweet lean natural gas with methane mole fraction of 60 - 67%. Based on gas compositions, a new coefficient; the Voss Coefficient; for easy determination of water content of sweet natural gases, was developed.

Keywords: Sweet natural gas, Water content charts, CPA-Equation of state, Voss Coefficient.

INTRODUCTION

Due to its occurrence in the reservoir in the presence of water and varying formation characteristics, natural gas is always full of impurities. These are mainly water and acid gases like CO_2 and H_2S . The acid gases are usually removed by a number of sweetening processes like the novel amine modified sorbent process (Anbia and Babaei, 2014) while the water can be removed by a number of dehydration processes. The water content of the gas is the amount of water contained in the gas or the amount of water the gas can hold at a particular condition of temperature and pressure. This water has to be kept low or controlled in order to avoid corrosion and other operational glitches that are consequences of water being present in the gas (Mohammadi, *et al.*, 2004). The knowledge of the water content is also a critical factor in determining whether or not gas hydrates will be formed in flow lines and other process equipment. Accurate evaluation and estimation of the amount of water contained in the gas, is of paramount importance in the design of an efficient gas dehydration, water treatment and water storage facilities.

The amount of water the gas can hold largely depend on temperature, pressure, and composition. The effect of composition is more pronounced as pressure increases and when the gas contains CO_2 and H_2S (GPSA, 1998). This implies that the effect of composition on the water content of natural gases with insignificant amounts of CO_2 and H_2S can be assumed to be negligible. The effect of composition can be ignored when the specific gravity of the

lean sweet gas is close to that of methane and the water content can be assumed to depend solely on temperature and pressure (Chapoy, 2004).

However, sweet natural gases can have specific gravities that are not close to 0.55. In the various studies involving natural gases, the majority of published gas composition had always been that with a methane component greater than 70% (Chapoy, 2004). As a result, the majority of the water content charts and other predictive empirical and semi-empirical models were developed with these gas compositions. Lean sweet natural gases have been found to have compositions with a methane component lower than 70%. Table 1.

Composition	Tern	MT -5.
	Platform.	Niger
	NorthSea	Delta
	(81psi)	(256 psi).
C ₁	60.65	62.16
C_2	9.53	11.19
C_3	13.95	7.58
$i - C_4$	6.79	3.67
$n-C_4$		4.73
$i - C_5$	2.76	1.82
$n-C_5$		1.88
C_6	1.02	
C ₆₊		0.19
C ₇₊	0.78	
N_2	2.99	5.15
CO_2	1.53	1.63
H ₂ O		

Table 1. Natural Gas with Methane Component between 60 - 63%.

It is therefore imperative, to ascertain the accuracy and reliability of water content charts (which is the aim of this study) and other predictive empirical and semi-empirical models in determining the water content of sweet natural gases with a methane fraction below 70%.

LITERATURE REVIEW

Several apparatuses exist for the direct measurement of water content of natural gases. Some of the most common types generally used in the gas industry include:

- 1. The Drager Tube (Colour indicator or stain tubes)
- 2. The Dew Point Meter Device
- 3. Impedance Sensors
- 4. Hygrometers

The indirect methods of analysis include, the use of:

- 1. Correlations
- 2. Equations of State (EOS)
- 3. Charts

Direct Methods

The Drager Tube

The drager tube also known as the colour indicator tube or the length of stain tube provides a simple and fast way for water content measurement. The water content is measured by exposing the tube to the gas for a given period. This allows for a colour change due to a chemical reaction between the reagent in the tube and the moisture in the gas.

The measurement is a direct function of the flow rate, exposure time and the extractive technique. As a result, this method is prone to errors. Errors as high as 25 % have been observed in practice for this device (Cook, 2006). Hence it serves as a means for making rough estimates and shouldn't be totally relied on for measurements involving water content of natural gases.

The Chilled Mirror Device

The chilled mirror device popularly known as the bureau of mines chilled mirror apparatus, measures the liquid condensation temperatures of the gas directly. This measured value of temperature is then converted to water content by appropriate correlations. It consists of a mirror which is cooled by coolant e.g. liquid propane. As the gas flows into the device and gets to the mirror, the mirror is cooled gradually. The temperature at which the first dew appears on the mirror is known as the dew point temperature. The condensation of the dew on the mirror is observed manually or automatically.

The mirror temperature is usually measured by a resistance thermometer attached to the reverse side of the mirror. Depending on the kind of set-up, this method can measure dew point temperatures from -99.6 to 80.3 °F with good accuracy (Chapoy, 2004).

The accuracy of this device is a function of the experience of the operator. Hence dew point measurement using the manually operated chilled mirror device is said to be subjective and require operator expertise. Despite the subjective nature of the results from this device, it is still one of the most widely used and precise devices for dew point determination (McKeogh, 2000). The advantages and disadvantages of using the Chilled Mirror Device can be seen in Table 2.

Pros	Cons
High Precision (within ± 0.1 to 0.5° C)	Limited by cooling capacity
Measure Dew point directly	Requires containment in a purged enclosure
Long term stability (5 - 20 years)	Not specific to water. Other gases may condense
Some models can measure at process pressure	Cannot measure low frost point accurately.

Table 2: Pros and Cons of the Chilled Mirror Device.

The Impedance Sensors

This device comprises two metal parts which acts as the electrodes of a capacitor consisting of an inert material with two dielectric layers. The most widely used of the impedance sensors are the aluminium oxide types. The water vapour in the gas is measured when the number of molecules adsorbed causes a change in the dielectric constant of the sensor. The sensor impedance is then correlated to the water concentration. Table 2 shows the advantages and disadvantages of using the Impedance Sensors.

Pros	Cons	
Can be used in hazardous area	High response time after process upsets	
Can be installed at long distances from the analyzer.	Affected by contaminants such as gycols and sulphur compounds.	
No adjustments are required for changes in gas composition	Calibration must be done annually.	

Table 3: Pros and Cons of Impedance Sensors

Hygrometers

The Tuneable diode laser absorption spectroscopy (TDLAS) hygrometer is one of the most precise hygrometers in use for water content measurement when precision and accuracy are required (Longman *et al.*, 2011) It provides a means of continuously measuring water vapour in natural gas. Its principle is based on passing light through a gas sample and then measuring the amount of light absorbed at the given wavelength (Beer – Lambert's Law).

Typical TDLAS hygrometers measure water content of natural gases with accuracy of within 2 %, using fundamental principles for measurement. It is immune to surface degrading. Table 3 shows the advantages and disadvantages of using the TDLAS Hygrometer.

Table 4: Pros and Cons of TDLAS Hygrometer			
Pros	Cons		
Very fast response	Relatively expensive		
Long term stability	Must be calibrated with a test gas with similar composition.		
Not affected by contaminants such as glycols.	Measurement is made close to atmospheric pressure		

An overall performance analysis was done by McKoegh (2000) to ascertain the suitability of the devices used for water content measurement as described above.

	Α	В	С
Range	1	5	3
Precision	5	2	4
Stability	5	2	5
Speed of Response	3	2	5
Maintenance	3	3	5
Cost	1	5	1

 Table 4: Performance of Selected Water Content Measuring Devices (McKoegh, 2000)

Where 5 = Most Desirable, 1 = Least Desirable

A = Chilled Mirror B = Impedance Sensors C = TDLAS Hygrometer

Indirect Methods Correlations

Some of these correlations emanated from fitting data from experiments (Zhu *et al.*, 2003), (Behr, 1983) and (Kazim, 1996), while others were developed using data from charts, (Sloan, 1998), (Ning *et al.*, 2000), (Khaled, 2007), (Bahadori *et al.*, 2009) and (Ghiasi and Bahadori, 2014) or data from phase equilibrium of water – hydrocarbon systems like Saturated vapour pressure model (Wang,1994) the Modified ideal model (Tohidi, 1995) and the Simplified Thermodynamic Model (Bukacek, 1959).

Most of these correlations were developed with a gas composition of methane mole fraction above 70 % or with data obtained from the McKetta and Wehe chart (methane mole fraction above 70 %). Most of these correlations, however, have a limited range of validity when it comes to gas composition, pressure, and temperature ranges.

Equations of State (Eos)

For the estimation of the amount of water (water content) contained in natural gases, Eos models provide a large range of applicability (Folas, *et al.*, 2007). These models can cover a wider range of gas compositions, temperature, and pressure, making them very reliable. As a result, EoS models are often used to validate experimental water content as well as empirical and semi-empirical correlations. The GERG – Water EoS and the Cubic plus Association EoS, are two examples of equations of state tailor fitted to predict water – hydrocarbon properties with good accuracy.

The GERG – Water EoS, which is a modification of the Peng Robinson EoS, is currently used as a standard (ISO 18453: 2004) for converting water dew point temperatures of natural gases, to water contents. This EoS was reported (with unknown uncertainty) to have a working range of -50° C to 40° C; 1 to 300 bar, for gas compositions with methane component > 40 mole %, < 30 mole % CO₂ and < 1.5 mole % C₆₊.

The Cubic Plus Association (CPA) EoS, is known to predict water content of natural gases with high accuracy (Kontogeorgis *et al.*, 1996), while also determining the most thermodynamically stable phase (Water, ice or hydrates). Previous studies have shown that the CPA –EoS, can describe equilibrium water content in natural gases with better accuracy than the GERG – Water EoS, with a larger range of composition, pressure, and temperature (Torbjorn, *et al.*, 2008). For this study, the CPA – EoS, was used to validate the water content results obtained from the various charts.

Charts

This method of estimating water content of sweet natural gas, is one of the oldest among other methods. Its simplicity still makes it very popular in the natural gas industry (Torbjorn, *et al.*, 2008). These charts were generated mainly from numerous experimental data gathered over the years and from thermodynamic models. Some of these charts have been reproduced over time to account for the presence of high gravity components and salinity in the gas. Examples of charts used in estimating the water content of sweet natural gases include;

- 1. Torbjørn's Chart (2008)
- 2. McKetta and Wehe's Chart (1958)

- 3. Katz's Chart (1959)
- 4. Campbell's Chart (2004)
- 5. Gordon's Chart (2003)
- 6. Guo and Ghalambor's Chart (2005)

Apart from the chart by Torbjørn, which was developed from the CPA –EoS thermodynamic model, all other charts were developed from experimental data gathered over the years. The Torbjørn chart has two sections for water content prediction. The bold line section (equilibrium with water) and the thin line section, which predicts water content of natural gas in equilibrium with hydrates. The McKetta and Wehe, and the Gordon charts are quite similar and account for the presence of heavy ends and salinity as well as provide information for metastable regions. The Guo and Ghalambor chart was developed from the McKetta and Wehe chart to account for accuracy in interpolations as well as an extended water content working range. The Katz and Campbell charts have no indicated region on their charts, for metastable conditions and so it is assumed that the most stable phase was used to develop the charts.

All the water content charts are plots of water content versus temperature on a semi-log graph with corresponding isobars, except the Guo & Ghalambor chart, which is a plot of water content versus pressure, on a log-log graph, with corresponding isotherms. Table 2 show the properties of each chart. The working pressure range for most of the charts is 14.7 to 10,000 psi, except Torbjørn chart, which has a range of 14.7 to 7252 psi. The Katz chart, has the highest working Temperature range of -70 to 700 ⁰F and the Torbjørn chart, with the least range of -40 to 240 ⁰F. The estimated water content working range is highest for the Guo & Ghalambor chart, from 1 to 200,000 lb/MMScf and least for the Campbell Chart, from 1 to 10,000 lb/MMScf.

Table 5: Chart Properties				
Chart	Graph		Working	
Name	Туре		Range	
		Pressure	Temperature	Water
				Content
Guo &	log -	14.7 to	- 60 to $280 {}^{0}\text{F}$	1 to
Ghalambor	log	10,000		100,000
		psi		lb/MMScf
McKetta &	Semi -	14.7 to	- 60 to 280 0 F	1 to
Wehe	log	10,000		50,000
		psi		lb/MMScf
Katz	Semi -	14.7 to	- 70 to 700 0 F	1 to
	log	10,000		47,000
		psi		lb/MMScf
Campbell	Semi -	14.7 to	- 40 to 240 0 F	1 to
_	log	10,000		10,000
		psi		lb/MMScf
Gordon	Semi -	14.7 to	- 60 to 400 0 F	1 to
	log	10,000		50,000
		psi		lb/MMScf
Torbjørn	Semi -	14.7 to	- 50 to 212 0 F	1 to 624
-	log	7,252 psi		lb/MMScf

The McKetta and Wehe Chart have been reported to be a standard for the estimation of the water content of sweet natural gas, making it the most used of all the charts.

Majority of these charts, like McKetta and Wehe, Gordon, Guo and Ghalambor, and Torbjørn were reported to have been developed for natural gas composition with methane mole component greater than 70 % (Sharma and Campbell, 1969) and (Campbell, 1994). Information on whether these charts or other existing ones like that of Katz and Campbell are reliable in estimating water content of sweet natural gas with methane component less than 70 %, is hardly available in the literature. What appropriate chart should, therefore, be used for gas compositions with a methane component below 70 %?

METHODOLOGY

Temperature and pressure data with ranges of $10.5 \,{}^{0}\text{C}$ (50.9 ${}^{0}\text{F}$) to $17 \,{}^{0}\text{C}$ (62.6 ${}^{0}\text{F}$) and 64 psi to 465 psi respectively, obtained from published water content result of natural gases (NG 1, NG 2, NG 3 and NG 4) with methane fraction between 60 - 67% (Aimikhe, *et al.*, 2017), were used to estimate the water content values, using the various charts in this study. The GetData Graph Digitizer software was used to extract the required data points from the charts. The water content values obtained from the various charts where then recorded.

To ascertain the accuracy and reliability of the results from these charts, water content predictions by the CPA – EoS, in equilibrium with water, were first calculated and then used to validate the results from the charts. Published data were also plotted alongside the CPA – EoS results in this study, to further evaluate the reliability of the published experimental data. Figures 1 to 4, show the results.

Error Analysis

Two statistical models were used to ascertain the error margins of water content results obtained from the five (5) charts in this study, and that of the water content predictions from the CPA - EoS model. These models include:

I. Percentage Average Absolute Deviation (%AAD): Given as:

$$\% AAD = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{W_{CPA} - W_{Calculated}}{W_{CPA}} \right| \times 100 \tag{1}$$

II. Standard Deviation (*SD*): Given as:

$$SD = \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left[\frac{W_{CPA} - W_{Calculated}}{W_{CPA}} \times 100 \right]^2}$$
(2)

Where N = number of data points and CPA = CPA EOS, W = Water content.

The results of the error analysis are given in Table 3.

Uncertainty Estimations

The calculated water content using the CPA – EoS had an uncertainty of 1%. While that of the estimated water content from the five charts had an uncertainty of 3 %.

RESULTS

The Figures 1 to 4, showed that all the charts followed similar trends with the CPA –EoS results and those from open literature, indicating a good relationship between water content calculations from the five charts, published experimental results and the CPA EoS model. The plots in Figures 1 to 4, was done on a Cartesian scale in order to observe the variation of the plotted parameters, clearly. This was because plots of dew point temperature and water content versus pressure had always been reported on a semi-log scale, which rather reduces the scatter thereby making it difficult to distinguish the error margins and thus, present the curves as single homogeneous straight lines.

On comparing the water content values obtained from the charts, with the CPA –EoS results, the accuracy of the existing water content charts was validated. Table 3 show the error margins between the water content estimated from the charts, compared with that obtained from the CPA – EoS. The Gordon's chart gave an overall percentage AAD of 5.45, Guo & Ghalambor, 5.88; Katz, 5.98; Campbell, 6.00 and McKetta & Wehe, 7.1. The relatively high percentage AAD can be attributed to the following reasons:

- The range of dew point temperatures were close to the metastable region (that is the region where the gas is in equilibrium with hydrates) on the charts. This region has been reported to contain less amount of water than indicated on the charts. It has also been reported in open literature that some experimental water content data reported as data in equilibrium with water, could have actually been measured in equilibrium with hydrates .Since majority of the charts were developed from empirical data, obtained from experimental analysis, it is most likely that erroneous values were reported by the charts in and around this metastable region.
- Errors due to interpolations from the charts and the accuracy of the GetData Graph Digitizer software, used for the extraction of data points from the charts.

The McKetta &Wehe, as well as the Guo & Ghalambor (obtained using data points from the McKetta & Wehe chart) charts, were reported to have been developed from natural gases having a methane component greater than 70 %. Information on whether these commonly used charts or other existing charts can accurately predict water content of sweet natural gas with methane component less than 70 % was relatively scarce.

The relatively low average absolute deviations (less than 10 %) validates the use of the charts in the estimation of the water content of sweet natural gas with methane mole fraction between 60 - 67%, with some degree of accuracy.



Figure 1. Water Content of Charts versus Experiment and CPA- EoS for NG 1



Figure 3. Water Content of Charts versus Experiment and CPA- EoS for NG 3.



Figure 4. Water Content of Charts versus Experiment and CPA- EoS for NG 4

Table 0: Error Analysis			
Gas	Charts	% AAD	SD
Samples			
NG 1	McKetta &	4.8	5.3
	Wehe		
	Campbell	3.2	3.5
	Gordon	6.3	6.7
	Katz	5.4	5.9
	Guo &	1.7	1.9
	Ghalambor		
NG 2	McKetta &	7.3	8.0
	Wehe		
	Campbell	6.9	7.2
	Gordon	5.8	6.8
	Katz	7.7	9.4
	Guo &	5.0	5.8
	Ghalambor		
NG 3	McKetta &	8.5	8.5
	Wehe		
	Campbell	9.4	9.7
	Gordon	4.2	5.6
	Katz	7.0	8.9
	Guo & 9.0		9.2
	Ghalambor		
NG 4	McKetta &	7.8	8.5
	Wehe		
	Campbell	4.5	4.7
	Gordon	5.5	6.2
	Katz	3.8	4.2
	Guo &	7.8	8.0
	Ghalambor		

Table 6: Error Analysis

DISCUSSION

To understand why the water content charts originally developed with gas composition of methane component above 70 %, gave similar results with those of methane component below 70 %, dew points and water content data, for these categories of gas samples were plotted and compared. Figures 7 showed that the dew points of gas samples with methane component below 70 % (NG 1 to NG 4) were approximately the same when compared to

samples with methane component above 70 % (NG 5 to NG 7) (Aimikhe, *et al.*, 2017). Figure 10 show similar results for water content. This clearly indicated that irrespective of the methane mole component (greater or lower than 70%), sweet natural gases will have relatively the same water dew points and water contents at the same pressures.



Figure 7: Comparison of water dew point temperatures for NG 1 to NG 7



Figure 10: Comparison of sample water contents of NG 1 to NG 7

The Voss (V) Coefficient

Brooks *et al.*, (1951), reported that the solubility of sweet natural gas in water is mostly influenced by the solubilities of methane, ethane, propane and butane components in water and that the solubility of the heavier components is very low and relatively insignificant. As the mole fraction of methane decreased, that of ethane, propane and butane increased for all the gas compositions in this study (70 % \leq CH₄ \leq 70 %). Also, for all cases of gas

composition considered in this study, the combined mole fraction of methane through butane was found to be approximately $\geq (0.9)$ 90 %, no matter how their mole fractions varied.

This relatively similar combined mole fraction (algebraic sum of the mole fractions of methane, ethane, propane and butane) of approximately 0.9 to 1, explains why the water content of the gas samples with methane component less than 70 %, was relatively the same with samples with methane component greater than 70 %.

This combined mole fraction which is the algebraic sum of the mole fractions of methane through butane has been proposed to be the Voss coefficient, V.

Mathematically, the Voss coefficient is given as:

$$V = n \sum_{i=1}^{4} c_i \tag{3}$$

Where

n = number of moles, i = ith component and C = carbon atoms.

Hence sweet natural gases with a Voss coefficient of approximately 0.9 (90 %) or greater, at the same pressures, will have relatively the same water content (provided CO_2 mole fraction is below 4 % and no H_2S is present). Therefore, for sweet natural gases with Voss coefficients of 0.9 or greater, an appropriate correlation or chart for determining lean sweet water content can be used for predicting the water content of the gas.

CONCLUSIONS

- 1. When used with care, The McKetta and Wehe, Campbell, Gordon, Katz, and the Guo and Ghalambor charts, are recommended for use in estimating water content of sweet lean natural gas with methane mole fraction of 60 67%.
- 2. The water content of gas samples with methane component less than 70 % are similar to those with methane component greater than 70 %.
- 3. A new coefficient known as the Voss Coefficient, for easy determination of water content of sweet natural gas has been developed.

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