Prediction of Moisture Content of Natural Gases Using Simple Arrhenius-type Function

Research Article

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Abstract: Natural gas extracted from underground reservoirs is saturated with water. The accurate prediction of moisture content in natural gas is extremely important. The presence of water vapor can lead to potentially disastrous consequences. The lifetime of a pipeline is governed by the rate at which corrosion occurs, which is directly linked to the available moisture in the gas resulting in oxidation. In addition, the formation of hydrates due to presence of water in natural gas can lead to safety hazards to production/transportation systems and to substantial economic risks. In this paper, an attempt has been made to develop an easy-to-use Arrhenius-type asymptotic exponential function combined with the Vandermonde matrix to arrive at an appropriate estimation of saturated water content of sour natural gases for pressures up to 69000 kPa and the temperature range between 20 to 180°C. Percent average absolute deviation of the proposed method is found to be around 2%, demonstrating the excellent performance of the developed predictive tool. The tool will be of great practical value for chemical and petroleum engineers to have a quick check on the water content of sour natural gases at various temperatures and pressures without performing any experimental measurements.

Keywords: Natural gas • water content • Arrhenius function • predictive tool • Vandemonde matrix • Matlab program
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1. Introduction

Moisture removal is a key stage of natural gas conditioning and processing prior to sale and its efficiency is important in order to satisfy fiscal contractual obligations and to ensure that the gas is safe to transport and contains the right properties for subsequent use [1]. When the gas is produced there is a simultaneous production of water as well. Some of this water is produced water from

the reservoir directly [2]. In the transmission of natural gas, further condensation of water is problematic. It can increase pressure drop in the line, often leading to corrosion problems and gas hydrate formation [1, 2] which can reduce pipeline flow capacities, blockages and potential damage to process filters, valves and compressors. Such hydrates are caused by the combination of excessive water vapor with liquid hydrocarbons, which may condense out of the gas in the course of transmission to form emulsions that, under process pressure conditions, are solid masses. There are numerous methods available for determining water content of natural gases [3–8]. In some of these models the vapor pressure of pure water is required

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as an input. Poor estimates of the vapor pressure will lead to poor estimates of the water content [2]. For example Sharma and Campbell [9] proposed a method for calculating the water content of natural gas. This method is rather difficult to use for hand calculations. Firstly, it requires the compressibility factor of the gas mixture. Secondly, it requires the fugacity of pure water at system conditions. The chart given to estimate this value is only valid for temperatures between 80°F (26.7°C) and 160°F (71.1°C) and for pressure less than 2000 psia (13800 kPa). This method requires three fugacity calculations for a single water content estimate.

McKetta and Wehe [10] published a chart for estimating the water content of sweet natural gas. This chart has been modified slightly over the years and has been reproduced in many publications, most notably the Gas Processors and Suppliers Association (GPSA) Engineering Data Book [11]. To obtain the values in this study, the original chart was photo enlarged to double its original size. Even so, it is difficult to read the chart to an accuracy of more than two significant figures [2]. The McKetta-Wehe chart is not applicable to sour gas, and there have been corrections proposed to make the chart applicable to these systems [12, 13]. In addition, Kobayashi et al. [7] presented a correlation for the curves plotted in the McKetta-Wehe chart. Their equation is quite complicated and it is only applicable for temperatures up to 120°F (48.9°C) and to 2000 psia (13800 kPa) [14].

For these above-mentioned reasons, the water content of sour natural gases is an important engineering consideration. Therefore, there is an essential need to develop a practical, reliable and easy-to-use method for practice engineers for the rapid estimation of the water content of sour natural gases to ensure successful, efficient and reliable gas transmission and processing plant operations.

2. Development of the predictive tool

Developing new predictive tools to minimize the complex and time-consuming calculation steps for estimating sour gas water content is an essential need. As most simulations require simultaneous iterative solutions of many nonlinear and highly coupled sets of equations, it is apparent that a mathematically compact, simple and reasonably accurate equations containing few tuned coefficients would be preferable for computationally intensive simulations [15]. In fact, the development of practical correlations by a small modification to the well-known Vogel-Tammann-Fulcher (VTF) (Vogel [16], Tammann and Hesse [17], Fulcher [18]) and Arrhenius [19] equation was

the primary motivation for the present paper, which nevertheless, yields predictive tools with accuracy comparable to that of the existing rigorous simulations. The present study discusses the formulation of such a novel and simple predictive tool which can be of significant importance to engineers to accurately estimate sour gas water content. Matlab [20] technical computing language and Vandermonde matrix can be used to adjust the parameters of predictive tool.

The primary purpose of the present study is to accurately estimate the water content of sour gases (W) as a function of temperature and pseudo H₂S mole fraction (y). This is done by a simple predictive tool using an Arrhenius-type asymptotic exponential function with a small modification of the Vogel-Tammann-Fulcher (VTF) equation (Vogel [16], Tammann and Hesse [17], Fulcher [18]) combined with the Vandermonde matrix and using Matlab technical computing language [15]. This is important as such an accurate and mathematically simple correlation the water content of sour gases (W) is required frequently for quick engineering calculations to avoid the additional computational burden of complicated calculations. The Vogel-Tammann-Fulcher (VTF) equation (Vogel [16], Tammann and Hesse [17], Fulcher [18]) is an asymptotic exponential function that is given in the following general form [21]:

$$\ln f = \ln(f_c) - \frac{E}{R(T - T_c)} \quad (1)$$

In equation 1, f is a properly defined temperature-dependent parameter, the units for which are determined individually for a certain property; f_c is a pre-exponential coefficient, having the same unit of the property of interest; T and T_c are the actual temperature and the characteristic-limit temperature, respectively (both given in degrees Kelvin); E is referenced as the activation energy of the process causing parameter variation (given in units of J/kmol); and R is the universal gas constant (R) 8.314 J/(kmol K)). A special case of the Vogel-Tammann-Fulcher (VTF) equation (Vogel [16], Tammann and Hesse [17], Fulcher [18]) for $T_c = 0$ is the well-known Arrhenius [19] equation.

For the purpose of this application which involves the correlation of density and vapor pressure of aqueous methanol or glycols solutions as a function of temperature, the Vogel-Tammann-Fulcher (VTF) equation (Vogel [16], Tammann and Hesse, [17], Fulcher [18]) has been modified in the following form by adding second-order and third order terms [15, 21].

$$\ln f = \ln f_c + \frac{b}{T - T_c} + \frac{c}{(T - T_c)^2} + \frac{d}{(T - T_c)^3} \quad (2)$$

In equation 2, T_c has been considered zero to convert equation 2 to the well-known Arrhenius [19] equation type.

$$\ln f = \ln f_c + \frac{b}{T} + \frac{c}{T^2} + \frac{d}{T^3} \quad (3)$$

The required data to develop this correlation includes the reported data [11], for the water content of sour gases (W) [11] as a function of temperature and pseudo H_2S mole fraction (y). The following methodology using Vandermonde matrix and Matlab [20] technical computing language have been applied to develop this correlation.

2.1. Vandermonde matrix

Vandermonde matrix is a matrix with the terms of a geometric progression in each row, i.e., an $m \times n$ matrix [22].

$$V = \begin{bmatrix} 1 & \alpha_1 & \alpha_1^2 & \dots & \alpha_1^{n-1} \\ 1 & \alpha_2 & \alpha_2^2 & \dots & \alpha_2^{n-1} \\ 1 & \alpha_3 & \alpha_3^2 & \dots & \alpha_3^{n-1} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 1 & \alpha_m & \alpha_m^2 & \dots & \alpha_m^{n-1} \end{bmatrix} \quad (4)$$

Or

$$V_{i,j} = \alpha_i^{j-1} \quad (5)$$

For all indices i and j . The determinant of a square Vandermonde matrix (where $m = n$) can be expressed as [22]:

$$\det(V) = \prod_{1 \leq i < j \leq n} (\alpha_j - \alpha_i) \quad (6)$$

The Vandermonde matrix evaluates a polynomial at a set of points; formally, it transforms coefficients of a polynomial $a_0 + a_1x + a_2x^2 + \dots + a_{n-1}x^{n-1}$ to the values the polynomial takes at the point's α_i . The non-vanishing of the Vandermonde determinant for distinct points α_i shows that, for distinct points, the map from coefficients to values at those points is a one-to-one correspondence, and thus that the polynomial interpolation problem is solvable with unique solution; this result is called the unisolvence theorem [23].

Thus, these are useful in polynomial interpolation, since solving the system of linear equations $Vu = y$ for u with V an $m \times n$ Vandermonde matrix is equivalent to finding the coefficients u_j of the polynomial(s) [23]

$$P(x) = \sum_{j=0}^{n-1} u_j x^j \quad (7)$$

of degree $\leq n - 1$ which has (have) the property:

$$P(\alpha_i) = y_i \quad \text{for } i = 1, \dots, m. \quad (8)$$

The Vandermonde matrix can easily be inverted in terms of Lagrange basis polynomials: each column is the coefficients of the Lagrange basis polynomial, with terms in increasing order going down. The resulting solution to the interpolation problem is called the Lagrange polynomial [23].

2.2. Approach to Developing the Predictive tool

The required data to develop this correlation includes the reported data for water content of sour gases (W) [11] as well as temperature and pseudo H_2S mole fraction (y). Equation 9 provides pseudo H_2S mole fraction (y) as a function of CO_2 and H_2S mole fractions. The water content of sour natural gas is predicted rapidly by proposing a novel correlation. The following methodology using Matlab [20] and Vandermonde matrix has been applied to develop this predictive tool.

For a given pressure, water content of sour gases (W) are first correlated as a function of temperature for various reported pseudo H_2S mole fraction (y). Then, the calculated coefficients for these polynomials are correlated as a function of pseudo H_2S mole fraction (y). The derived polynomials are applied to calculate new coefficients for equation (10) to predict water content of sour gases (W). Table 1 shows the tuned coefficients for equations (11) to (14) for pressure at 6900, 14000, 21000, 41000 and 69000 kPa (abs).

$$y = y_{H_2S} + 0.75 \times y_{CO_2} \quad (9)$$

$$\ln(W) = a + \frac{b}{T} + \frac{c}{T^2} + \frac{d}{T^3} \quad (10)$$

Where:

$$a = A_1 + B_1y + C_1y^2 + D_1y^3 \quad (11)$$

$$b = A_2 + B_2y + C_2y^2 + D_2y^3 \quad (12)$$

$$c = A_3 + B_3y + C_3y^2 + D_3y^3 \quad (13)$$

$$d = A_4 + B_4y + C_4y^2 + D_4y^3 \quad (14)$$

$$W = W_1 + (P - P_1) \frac{(W_2 - W_1)}{(P_2 - P_1)} \quad (15)$$

In brief, the following steps are repeated to tune the correlation's coefficients.

Table 1. Tuned coefficients used in equation 11-14 to correlate water content as a function of temperature at 6900, 14000 kPa (abs) , 21000, 41000 and 69000 kPa (abs).

Value for 69000 kPa	Value for 41000 kPa	Value for 21000 kPa	Value for 14000 kPa	Value for 6900 kPa	Coeff
$1.1487249695996 \times 10^1$	$1.748930534066 \times 10^1$	8.8752257764411	$1.8110838211653 \times 10^1$	-8.6992897364476	A_1
$1.8235899614239 \times 10^2$	$-6.6857234321439 \times 10^1$	$7.2359055865547 \times 10^1$	$-3.3553927198229 \times 10^1$	$-4.6967311684626 \times 10^1$	B_1
$-1.288486787033 \times 10^3$	$1.0790113323879 \times 10^3$	$1.0335271494007 \times 10^2$	$1.6824427204283 \times 10^2$	$3.1315261544295 \times 10^2$	C_1
$2.1158986161079 \times 10^3$	$-2.2762195961481 \times 10^3$	$-6.5301771606061 \times 10^2$	$-2.6948419542619 \times 10^2$	0	D_1
$-2.6543588470054 \times 10^3$	$-8.7901042066063 \times 10^3$	$5.1776138075660 \times 10^2$	$-8.5630661135216 \times 10^3$	$2.0088965397978 \times 10^4$	A_2
$-2.1165875865785 \times 10^5$	$6.678190417536 \times 10^4$	$-8.7971995837776 \times 10^4$	$3.0551218745808 \times 10^4$	$4.9646614809644 \times 10^4$	B_2
$1.4698504519682 \times 10^6$	$-1.176159078161 \times 10^6$	$-8.3722203514478 \times 10^4$	$-1.7056837565438 \times 10^5$	$-3.4189493136275 \times 10^5$	C_2
$-2.400952764466 \times 10^6$	$2.498247990701 \times 10^6$	$6.8032176760827 \times 10^5$	$2.8115260340764 \times 10^5$	0	D_2
$-7.5258032055602 \times 10^5$	$1.4302450445397 \times 10^6$	$-1.6646235148766 \times 10^6$	$1.385122323083 \times 10^6$	$-8.4283845988169 \times 10^6$	A_3
$8.1236523831462 \times 10^7$	$-2.177601844133 \times 10^7$	$3.5036420983709 \times 10^7$	$-8.6675428997521 \times 10^6$	$-1.7339466157663 \times 10^7$	B_3
$-5.5361784748092 \times 10^8$	$4.2432245600508 \times 10^8$	$1.833030185193 \times 10^7$	$5.5966077952265 \times 10^7$	$1.2339127230272 \times 10^8$	C_3
$8.9969938341627 \times 10^8$	$-9.078369462879 \times 10^8$	$-2.3174062571704 \times 10^8$	$-9.624968254877 \times 10^7$	0	D_3
$1.1064336815477 \times 10^8$	$-1.495941594688 \times 10^8$	$1.7742319902892 \times 10^8$	$-1.636288455096 \times 10^8$	$9.3484127541312 \times 10^8$	A_4
$-1.0161844621207 \times 10^{10}$	$2.4252810682628 \times 10^9$	$-4.4932538113089 \times 10^9$	$7.9328177772919 \times 10^8$	$2.0283228863636 \times 10^9$	B_4
$6.8764136066843 \times 10^{10}$	$-5.068992989058 \times 10^{10}$	$-6.4855702288926 \times 10^8$	$-5.955397398353 \times 10^9$	$-1.4729685977716 \times 10^{10}$	C_4
$-1.1126881236117 \times 10^{11}$	$1.0921229873138 \times 10^{11}$	$2.5791018846089 \times 10^{10}$	$1.086941710694 \times 10^{10}$	0	D_4

1. Correlate the water content of sour gases (W) as a function of temperature for the selected pseudo H₂S mole fractions (y).
2. Repeat steps 2 and 3 for other data and other pseudo H₂S mole fractions (y).
3. Correlate corresponding polynomial coefficients, which were obtained for different temperatures versus pseudo H₂S mole fraction (y), $a = f(y)$, $b = f(y)$, $c = f(y)$, $d = f(y)$ [see equations (11)-(14)].
4. Calculate the water content of sour gases (W) as a function of temperature and pseudo H₂S mole fraction from equations (10) and (14), respectively.
5. Calculate water content of sour natural gas using simple interpolation formula (equation 15) to various pressures.
6. The water content of sour gases at low pressures is approximately independent of composition, so equation 16 and Table 2 are suggested to calculate water content at 2100 kPa (abs).

$$\ln(W) = \alpha + \frac{\beta}{T} + \frac{\gamma}{T^2} + \frac{\theta}{T^3} \quad (16)$$

Equations 9-16 present the developed tool for predicting water content of sour natural gases, as a function of temperature, pseudo H₂S mole fractions and pressures. The tuned coefficients are also given in Table 1 can be

Table 2. Tuned coefficients used in equation 16 to correlate water content as a function of temperature at 2100 kPa (abs).

Coefficients	Value
α	$-1.7726834385506 \times 10^1$
β	$3.0306586238333 \times 10^4$
γ	$-1.1989223586817 \times 10^7$
θ	$1.3598977939352 \times 10^9$

also retuned if more accurate data are available in the future.

The predictive tool proposed in is simple and has an unique expression which is non-existent in the literature. In addition, logarithmic function is selected to develop the correlation, as these functions are smooth and well-behaved (i.e. smooth and non-oscillatory) equations which should allow for more accurate predictions [15].

3. Results

Figure 1 shows the developed Matlab-based predictive tool. Figures 2 to 6 show the obtained results of the new proposed predictive tool for predicting the water content of sour natural gases at 6900, 14000, 21000, 41000 and 69000 kPa (abs) respectively. As shown, the obtained results show good agreement with the reported data. Table 3 shows that the proposed predictive tool has good agreement with the reported data [11] and the average absolute deviation is around 2%.

Table 3. Comparison of obtained results of new proposed predictive tool for predicting water content of sour gases with the reported data [11].

Pressure kPa	Temperature °C	Pseudo H ₂ S mole fraction (y)	Calculated water content $\frac{mg}{Sm^3}$	Reported water content, [11] $\frac{mg}{Sm^3}$	Absolute deviation percent
6900	32	0	0.6185	0.6	3.08
6900	66	20	3.9133	4	2.16
6900	132	40	40.0084	40	0.21
14000	30	0	0.3919	0.4	2.02
14000	44	10	0.9144	0.9	1.6
14000	77	20	4.0774	4	1.93
14000	128	30	28.3998	30	5.33
14000	169	40	57.7452	60	3.90
21000	38	0	0.4653	0.5	6.94
21000	50	10	1.0476	1	4.76
21000	98	20	7.0879	7	1.25
21000	103	30	9.2284	9	2.53
21000	164	40	40.3141	40	0.78
41000	32	0	0.29478	0.3	1.74
41000	47	10	0.7782	0.8	2.72
41000	86	20	3.9497	4	1.25
41000	100	30	7.1196	7	1.70
41000	158	40	30.0236	30	0.08
69000	27	0	0.19827	0.2	0.87
69000	48	10	0.705348	0.7	0.76
69000	91	20	3.9686	4	0.78
69000	109	30	8.07455	8	0.93
69000	162	40	29.897	30	0.34
Average absolute deviation percent (AADP)					2.07

Figure 1. Developed Matlab-based [15] predictive tool for calculating sour gas water content.

Figure 2. Performance of proposed predictive tool for estimation of water content of sour natural gases at 6900 kPa (abs).

Figure 5. Prediction of water content of sour natural gases and acid gas mixtures at 41000 kPa (abs).

Figure 3. Prediction of water content of sour natural gases and acid gas mixtures at 14000 kPa (abs).

Figure 6. Prediction of water content of sour natural gases and acid gas mixtures at 69000 kPa (abs).

Figure 4. Prediction of water content of sour natural gases and acid gas mixtures at 21000 kPa (abs).

The proposed simple method covers water content for temperatures range between 25–175°C, and pseudo H₂S mole fraction up to 0.45 as well as pressure up to 69000 kPa (abs). Sample calculations shown here clearly demonstrate the simplicity of the proposed predictive tool and the benefits associated with such empirical estimations. The approach is of practical significance for natural gas processing industries and gas reservoir engineering in terms of assessing operational issues. In particular, the proposed correlation gives an advance indication of key parameters which could potentially enable practice engineers to take appropriate remedial measures in the design of facilities for natural gas production, transmission, and processing.

3.1. Sample calculation for practice engineers

Determine the saturated water content of a mixture containing 80% CH₄ and 20% CO₂ at 70°C and 13800 kPa (abs).

Sample solution:

$y = y_{H_2S} + 0.75 \times y_{CO_2} = 0 + 0.75(0.2) = 0.15$ (from equation 9).

$a = -8.69845264$ (from equation 11)

$b = 1.9843321663 \times 10^4$ (from equation 12)

$c = -8.253000895 \times 10^6$ (from equation 13)

$d = 9.0767177386 \times 10^8$ (from equation 15)

$4.4993 \frac{mg}{Sm^3}$ at 6900 kPa. (from equation 10)

Now, repeat the calculations for pressure=14000 kPa

$a = 2.276836397 \times 10^1$ (from equation 11)

$b = -1.44306367582 \times 10^4$ (from equation 12)

$c = 3.776501918013 \times 10^6$ (from equation 13)

$d = -4.728356771532 \times 10^8$ (from equation 14)

$2.95842 \frac{mg}{Sm^3}$ at 14000 kPa. (from equation 10)

After interpolation, the water content of natural gas at 13800 kPa will be:

$W = 2.95842 + (13800 - 14000)(4.4993 - 2.95842)/(6900 - 14000) = 2.99 \frac{mg}{Sm^3}$ (from equation 15)

This is a classic example showing how the information evolving out of the proposed predictive tool can be used to understand and estimate the water content of sour gases (W). The proposed tool is easy to use which employs simple algebraic equations and can be solved by a simple calculator quickly by any water practitioner without going into the complicated principles of thermodynamics and associated expressions.

4. Conclusions

Presented in this paper, a simple-to-use predictive tool for accurate estimation of water content of sour natural gas mixtures containing up to 40 mole percent acid gas

components was developed. Predicted results show good agreement with the reported data, wherein the new developed method works for pressures up to 69000 kPa (abs), temperatures from 25 to 180 °C and pseudo H₂S mole fractions up to 0.4. The proposed correlation has excellent association with the reported data. Estimations from the proposed tool have been compared with reported data and found good agreement with average absolute deviation being less than 2.1%. The proposed tool appears to be superior owing to its accuracy and simple background, wherein the relevant coefficients can be retuned quickly if new and more accurate data are available in the future. The example shown for the benefit of natural gas practitioners clearly demonstrates the usefulness of the proposed tool for the practice engineers. It is expected that our efforts in this investigation will pave the way by arriving at an accurate measure of the water content of sour gases at various conditions which can be used by the gas processing industries personnel for monitoring the operational parameters periodically in the design of facilities for the natural gas production, transmission, and processing.

4.1. Nomenclature

A: Tuned coefficient

B: Tuned coefficient

C: Tuned coefficient

D: Tuned coefficient

E: The activation energy of the process causing parameter variation (J/kmol),

f: properly defined temperature-dependent parameter, the units for which are determined individually for a certain property.

f_c: pre-exponential coefficient, having the same unit of the property of interest

i: index

j: index

m : matrix row index for $m \times n$ matrix

n:matrix column index for $m \times n$ matrix

P: Pressure, kPa(abs)

R : Universal gas constant (R) 8.314 J/ (kmol K)

T : Temperature, K

T_c : Characteristic-limit temperature, K

u : coefficient of polynomial

V : Vandermonde matrix

W : Sour Gas water content, mg/(Standard cubic meter)

y :Pseudo H_2S mole fraction

y_{CO_2} :Carbon dioxide mole fraction

y_{H_2S} :Hydrogen sulfide mole fraction

y : Pseudo H_2S mole fraction

α : Matrix element

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