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Use of Artificial Neural Networks for Estimating Water Content of Natural Gases

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Many thermodynamic models and correlations/charts are available that can estimate the water content of natural gases. The available methods normally have lower accuracy in regard to predicting the water content under low-temperature conditions and require further verification, because, during the development of the original predictive methods, experimental data that describe the phase equilibrium in water−hydrocarbon systems at low temperatures were not available. This is partially due to the fact that the water content of gases is indeed very low at low temperatures and high pressures, and, hence, it is generally very difficult to measure, because of, for example, adsorption problems in the sample transfer line or the analytical device. In this communication, an alternative method based on a feed-forward artificial neural network with a modified Levenberg−Marquardt algorithm is used to estimate the water content of natural gases, which assures high flexibility of the functional form for the regression. The method has been developed using recent experimental water content data, especially at low temperatures and near/inside the hydrate region. Experimental data that are not used in the development of this method have been used to examine the reliability of this method. The results are also compared with predictions of other predictive techniques. It is shown that the predictions of this method are in acceptable agreement, which demonstrates the reliability of the artificial neural network method for estimating the water content of natural gases.

1. Introduction

Accurate knowledge of the phase behavior in water−hydrocarbon systems is of great interest in the petroleum industry, because petroleum fluids are normally saturated with water, under reservoir conditions. The dissolved water may condense during production, transportation, and processing, which leads to the formation of gas hydrate/ice and corrosion/two-phase flow problems. The design and dimensioning of the production, transportation, and processing facilities can be also optimized if one has reliable and accurate information on the water−hydrocarbon phase behavior. The predictive methods for estimating the water content of natural gases are either empirical/semiempirical correlations and charts or thermodynamic models.[1,2] The main advantage of empirical/semiempirical correlations and charts is the availability of input data and the simplicity of the calculations, which can be performed using charts or hand-held calculators/Excel worksheets.[2−4] Modeling water−hydrocarbon phase equilibrium via conventional thermodynamic models requires the use of many adjusted parameters. These models usually require considerable efforts to find an appropriate relationship for fitting experimental data. However, the available predictive methods have lower accuracy in predicting the water content of gases at low temperatures and require further verification.[1−4] Therefore, there is still a need for simple, yet robust, predictive techniques for estimating the water content of natural gases.[2−4]

The objective of this work is to show the capability of artificial neural networks (ANNs) for estimating the water content of natural gases, especially at low temperatures. To our knowledge, this method has not been previously reported for estimating the moisture content of natural gases and can provide fast and accurate estimation of the water content of natural gases. Among the various ANNs reported in the literature, the feed-forward (back-propagation) neural network (FNN) method with a modified Levenberg−Marquardt algorithm[5,6] is used, which is known to be effective to represent the nonlinear relationships between variables in complex systems and can be regarded as a large regression method between input and output variables.[7] To develop this method, reliable and recent literature data are used. The developed method is then used to predict independent experimental data (which are not used in the development of this method) and the predictions are also compared with the results of other predictive tools. The results are shown to be in acceptable agreement, which demonstrates the ability and reliability of the ANN-based method to estimate the water content of natural gases.

2. Artificial Neural Network

A detailed description of neural networks is given elsewhere.[5] ANNs mimic the behavior of biological neurons and learn by trial and error.[8] These methods have large numbers of computational units connected in a massively parallel structure[9] and do not require an explicit formulation of the mathematical or physical relationships of the handled problem.[5] The ANNs are first subjected to a set of training data that consists of input data and the corresponding outputs. After a sufficient number of training iterations, the neural network learns the patterns in the data fed to it and it creates an internal model, which it uses to make predictions for new inputs.[8] The accuracy of model representation is dependent directly on the architecture of the neural network.

The most commonly used ANNs are the FNNs and the radial basis function (RBF) networks.[10] Feed-forward neural networks

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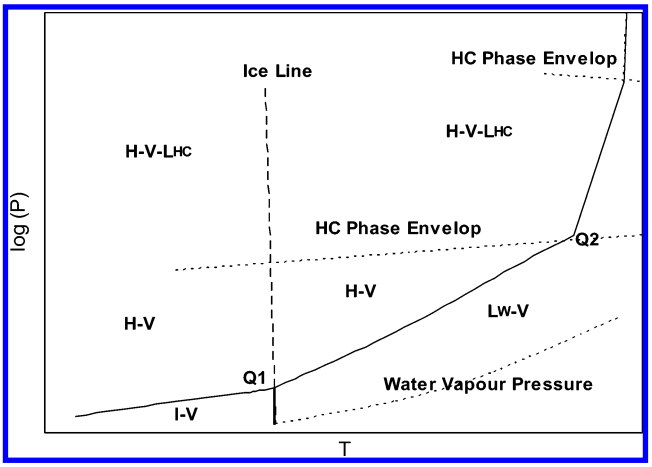

Figure 1. Typical pressure−temperature ($P-T$) diagram for a water (limiting reactant)−hydrocarbon system. Figure legend: H, hydrate; HC, hydrocarbon; I, ice; L_{HC}, liquid hydrocarbon; L_W, liquid water; V, vapor; Q_1, lower quadruple point; and Q_2, upper quadruple point.

are the most frequently used and are designed with one input layer, one output layer, and hidden layers.[9] The number of neurons in the input and output layers equals to the number of inputs and outputs, respectively. The disadvantage of FNNs is the determination of the ideal number of neurons in the hidden layer(s); a few neurons produce a network with low precision and a higher number of neurons leads to overfitting and poor-quality interpolation and extrapolation. The use of techniques such as Bayesian regularization, together with a Levenberg−Marquardt algorithm, can help overcome this problem.[9,10] The RBFs use a Bayesian decision strategy, and each input normally has its distance from the input vector calculated in the first layer. This process results in a vector whose elements indicate how close the input is, in relation to the training input. The second layer produces a vector of probabilities that will be used in the determination of the input class.[10]

In this work, the FNN method with a single hidden layer[9] is devoted to the computation of the logarithm of water content (output neuron), which is a function of pressure and an inverse function of temperature and gas gravity (input neurons), because the logarithm of water content versus the inverse of temperature at a given pressure has a linear behavior. In this method, each neuron of the hidden layer performs two tasks: a weighted summation of its input and the application of the transfer function to this summation.[7] The neuron of the output layer simply performs a weighted summation of the outputs of the hidden neurons.[7] Three types of transfer functions were tested: the exponential sigmoid, tangent sigmoid, and linear. The former transfer function yields better results. The bias is set to 1, to add a constant to the weighted sum for each neuron of the hidden layer.[7] The mathematical form for the water content can be expressed by the following equation:

$$\log(y_W) = \sum_{i=1}^{n} w_i f(\upsilon_i) \tag{1}$$

where

$$f(\upsilon_i) = \frac{1}{1 + e^{-\upsilon_i}} \tag{2}$$

and

$$\upsilon_i = \frac{w_{1i}}{T} + w_{2i}P + w_{3i}\gamma + w_{4i} \tag{3}$$

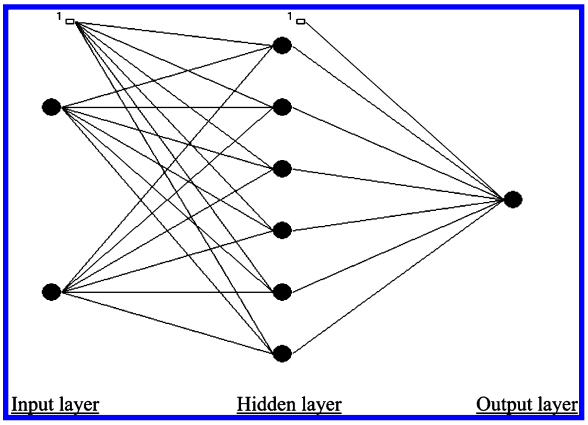

Figure 2. Architecture of the neural network method used to estimate the water content of natural gases in equilibrium with liquid water or ice. Items marked "1" represent bias, whereas items marked by a solid circle (●) represent neurons. The output neuron is the logarithm of the water content, whereas the input neurons are the pressure (P) and the inverse of temperature ($1/T$).

Table 1. Number of Neurons, Hidden Layers, and Data Used in This Method for Estimating the Water Content in Equilibrium with Liquid Water or Ice

type	value/comment
layer 1	2 neurons
layer 2	6 neurons
layer 3	1 neuron
number of hidden layers	1
number of parameters	25
number of data used for training	95
type of function	exponential sigmoid

where y, w, f, υ, T, P, γ, and n represent the mole fraction in the gas phase, weight, function, weighted sum of input to the hidden neuron i, temperature, pressure, gas gravity, and the number of neurons in the hidden layer, respectively. The subscripts W and i represent water and the number of hidden layers, respectively. As can be seen, the inputs that represent the independent variables enter the neurons of the input layers and then the transfer function $f(\upsilon_i)$ converts the inputs to outputs in the neurons. The number of neurons in the hidden layer can be varied by searching for both the lowest value of the minimized objective function and the generalizing capability of the ANN method for various conditions. In fact, by changing the number of neurons in the hidden layer, it is possible to change the mathematical form of the shape function with the

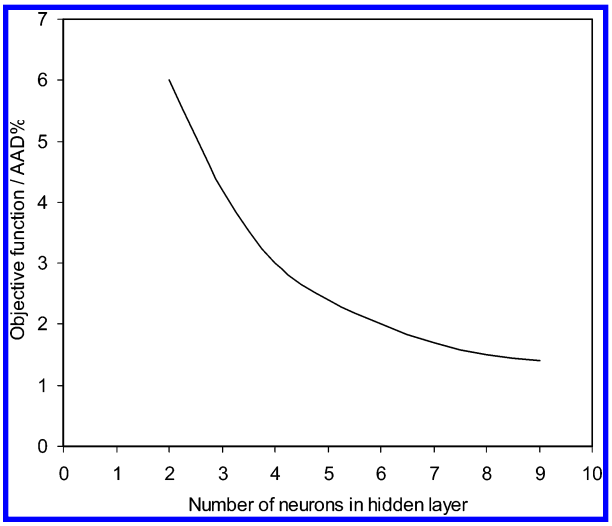

Figure 3. Objective function versus the number of neurons in the hidden layer.

Table 2. Experimental Data of the Learning Sets on Water Content of Methane in Equilibrium with Liquid Water Used for Developing This Method

reference	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	number of data points	AAD (%)[a]
Chapoy et al.[11]	277.80	297.90	0.491	4.374	22	2.7
Mohammadi et al.[1]	282.98	313.12	0.51	2.846	17	1.8
Althaus [12]	273.15	293.15	0.5	10	19	1.9
Rigby and Prausnitz[13]	298.15	373.15	2.35	9.35	12	1.2
Yokoyama et al.[14]	298.15	323.15	3	8	5	1.4
Gillespie and Wilson[15]	323.15	348.15	1.379	13.786	6	1.4
Kosyakov et al.[16]	273.16	283.16	1.01	6.08	5	4.4
Olds et al.[17]	310.93	377.59	2.67	13.81	9	1.7

[a] AAD (%) $= 1/N \sum_{i=1}^{N} |$(experimental value − calculated value)/(experimental value)$| \times 100$.

objective of obtaining higher accuracy of the final model.[9] Too few hidden neurons hinder the learning process and too many occasionally degrade the generalizing capability of the network.[7] The parameters w_{1-4i} (for $i = 1, ..., n$) in the summations, which are usually called the weights, are the fitting parameters of the ANN. These parameters can be determined by applying a least-squares regression procedure to a given set of experimental data. The fitting procedure, which is normally called the learning of the ANN, is performed using a modified Levenberg−Marquardt algorithm.[5,6,9] The objective function corresponding to the logarithm of water content is the sum of squares of relative deviations between the experimental and calculated values.

The Levenberg−Marquardt algorithm[5,6,9] consists of modifying the network's weight using the following equations:

$$w_j = w_{j-1} - [\bar{H} + \mu_j \bar{I}]^{-1} \nabla J(w_{j-1}) \tag{4}$$

with

$$\bar{H} = \sum_{k=1}^{n} \left(\frac{\partial \mathrm{err}^k}{\partial w_j} \right) \left(\frac{\partial \mathrm{err}^k}{\partial w_j} \right)^{\mathrm{T}} + \sum_{k=1}^{n} \left(\frac{\partial^2 \mathrm{err}^k}{\partial w_j \partial w_j^{\mathrm{T}}} \mathrm{err}^k \right) \tag{5}$$

where err^k, μ, J, N, $\bar{H}$, and $\bar{I}$ are the residue vector, the step values of the Levenberg−Marquardt algorithm,[5,6,9] the Jacobian matrix of the first derivative of global error to weight, the number of feed inputs, the Hessian matrix, and the identity matrix, respectively. The parameter err^k is defined by

$$\mathrm{err}^l = (\text{experimental value}) - (\text{calculated value}) \tag{6}$$

3. Results and Discussions

Figure 1 shows a typical pressure−temperature diagram for water−hydrocarbon systems. Most of the existing experimental data have been reported for the water content of gases in equilibrium with liquid water, and the experimental work that has been conducted to describe the water content of gases in equilibrium with gas hydrates or ice are limited in accuracy, because of the fact that metastable liquid water may extend well into the gas hydrate or ice regions.[2,4] The water content of gases in equilibrium with gas hydrates or ice is less than the water content of gases in equilibrium with metastable liquid water and therefore is difficult to measure, because the formation of hydrate or ice is a time-consuming process. The water content of gases in the hydrate region is also a strong function of gas composition.[2,4] The gas−ice phase equilibrium for sweet natural gases with very low nitrogen content can be reached at relatively low pressures. The maximum pressure at which the gas−ice phase equilibrium can be attained is ∼2.56 MPa, which corresponds to the hydrate formation conditions for methane near the quadruple point (Q).[2] Therefore, the difference between the water content of natural gases being in equilibrium with ice or metastable liquid water can be ignored for engineering purposes at temperatures that are not very low.

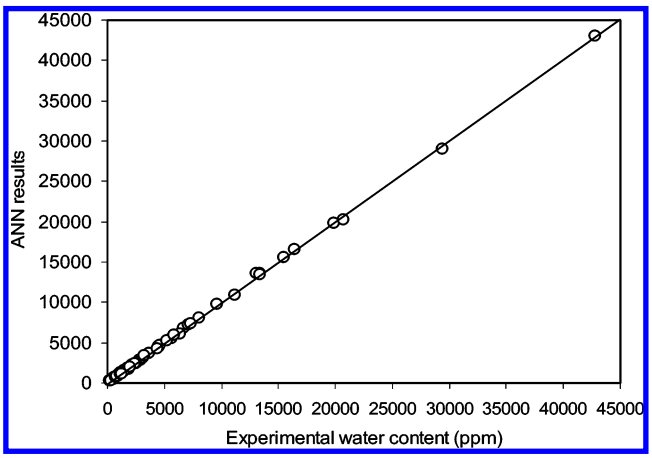

Figure 4. ANN results versus experimental data of the learning sets reported in Table 2.

3.1. Estimating the Water Content of Natural Gases in Equilibrium with Liquid Water or Ice. Because the water content of sweet gases with low concentrations of heavy hydrocarbons is approximately equal to the water content of methane, especially at low temperatures,[2−4] the method is therefore developed for the methane−water system and it is then used to predict the water content of natural gases. That is, the effect of gas gravity can be ignored for engineering purposes. The ANN method shown in Figure 2 and detailed in Table 1 with one hidden layer is devoted to the computation of the logarithm of water content as a function of pressure and an inverse function of temperature. Figure 3 shows the values of the objective function versus the number of neurons in the hidden layer. As can be seen, the number of hidden neurons was varied between 2 and 9 and the best value according to both the accuracy of the fit (minimum value of the objective function) and the predictive power of the neural network was determined to be 6. The water content data used in this work were obtained from a previously reported literature review,[1] where an overview of the experimental data available in the literature was provided. Table 2 shows the data used in the present study. A total of 95 data entries have been examined. As can be observed, temperatures are in the range of 273.15−377.59 K at pressures up to 13.81 MPa. The maximum percentage of average absolute deviation (AAD) is 4.4%. A preliminary study shows that the results should be sufficiently acceptable, because the input variables were well chosen (two input variables, i.e., temperature and pressure) and there are sufficient data to train the network and avoid the overfitting problem. (The best way to avoid the overfitting problem is to use a large amount of training data.) Figure 4 shows the experimental data reported in Table 2, versus ANN results. To

Table 3. Comparing the Predictions of This Method, the Semiempirical Approach,[2] and the Bukacek[18] Correlation with the Validation Data Sets for the Water Content of Various Natural Gases (NG*x*)

				Using ANN		Using the Semiempirical Method[2]		Using the Bukacek Correlation[18]	
T (K)	*P* (MPa)	gas gravity	experimental water content[12] (mol fraction)	predicted water content (mol fraction)	AD (%)[a]	predicted water content (mol fraction)	AD (%)[a]	predicted water content (mol fraction)	AD (%)[a]
				NG1					
273.15	0.5	0.5654	1.17×10^{-3}	1.21×10^{-3}	3.4	1.25×10^{-3}	6.9	1.24×10^{-3}	6.1
273.15	1.5	0.5654	4.26×10^{-4}	4.41×10^{-4}	3.5	4.39×10^{-4}	3.1	4.62×10^{-4}	8.5
278.15	0.5	0.5654	1.68×10^{-3}	1.75×10^{-3}	4.2	1.79×10^{-3}	6.6	1.82×10^{-4}	8.3
278.15	1.5	0.5654	6.05×10^{-4}	6.08×10^{-4}	0.5	6.25×10^{-4}	3.3	6.53×10^{-4}	7.9
283.15	1.5	0.5654	8.42×10^{-4}	8.82×10^{-4}	4.8	8.78×10^{-4}	4.3	9.11×10^{-4}	8.2
283.15	6	0.5654	2.51×10^{-4}	2.43×10^{-4}	3.2	2.68×10^{-4}	6.8	2.97×10^{-4}	18.3
288.15	1.5	0.5654	1.16×10^{-3}	1.21×10^{-3}	4.3	1.22×10^{-3}	5.2	1.25×10^{-3}	7.8
288.15	6	0.5654	3.56×10^{-4}	3.35×10^{-4}	5.9	3.69×10^{-4}	3.7	4.02×10^{-4}	12.9
288.15	10	0.5654	2.50×10^{-4}	2.41×10^{-4}	3.6	2.60×10^{-4}	4.0	2.88×10^{-4}	15.2
				NG2					
273.15	0.5	0.598	1.19×10^{-3}	1.21×10^{-3}	1.7	1.25×10^{-3}	5.0	1.24×10^{-3}	4.2
278.15	0.5	0.598	1.68×10^{-3}	1.75×10^{-3}	4.2	1.79×10^{-3}	6.6	1.82×10^{-3}	8.3
278.15	1.5	0.598	5.99×10^{-4}	6.08×10^{-4}	1.5	6.25×10^{-4}	4.3	6.53×10^{-4}	9.0
288.15	1.5	0.598	1.16×10^{-3}	1.21×10^{-3}	4.3	1.22×10^{-3}	5.2	1.25×10^{-3}	7.8
288.15	4	0.598	4.68×10^{-4}	4.84×10^{-4}	3.4	5.09×10^{-4}	8.8	5.44×10^{-4}	16.2
288.15	6	0.598	3.56×10^{-4}	3.35×10^{-4}	5.9	3.69×10^{-4}	3.7	4.02×10^{-4}	12.9
293.15	6	0.598	4.65×10^{-4}	4.76×10^{-4}	2.4	5.00×10^{-4}	7.5	5.39×10^{-4}	15.9
293.15	10	0.598	3.26×10^{-4}	3.32×10^{-4}	1.8	3.50×10^{-4}	7.4	3.83×10^{-4}	17.5
				NG3					
273.15	0.5	0.628	1.20×10^{-3}	1.21×10^{-3}	0.8	1.25×10^{-3}	4.2	1.24×10^{-3}	3.3
278.15	0.5	0.628	1.72×10^{-3}	1.75×10^{-3}	1.7	1.79×10^{-3}	4.1	1.82×10^{-3}	5.8
283.15	1.5	0.628	8.26×10^{-4}	8.82×10^{-4}	6.8	8.78×10^{-4}	6.3	9.11×10^{-4}	10.3
288.15	1.5	0.628	1.15×10^{-3}	1.21×10^{-3}	5.2	1.22×10^{-3}	6.1	1.25×10^{-3}	8.7
				NG4					
273.15	0.5	0.6326	1.19×10^{-3}	1.21×10^{-3}	1.7	1.25×10^{-3}	5.0	1.24×10^{-3}	4.2
278.15	0.5	0.6326	1.71×10^{-3}	1.75×10^{-3}	2.3	1.79×10^{-3}	4.7	1.82×10^{-3}	6.4
278.15	1.5	0.6326	5.91×10^{-4}	6.08×10^{-4}	2.9	6.25×10^{-4}	5.8	6.53×10^{-4}	10.5
283.15	1.5	0.6326	8.50×10^{-4}	8.82×10^{-4}	3.8	8.78×10^{-4}	3.3	9.11×10^{-4}	7.2
288.15	1.5	0.6326	1.17×10^{-3}	1.21×10^{-3}	3.4	1.22×10^{-3}	4.3	1.25×10^{-3}	6.8
288.15	4	0.6326	4.85×10^{-4}	4.84×10^{-4}	0.2	5.09×10^{-4}	5.0	5.44×10^{-4}	12.2
293.15	6	0.6326	4.70×10^{-4}	4.76×10^{-4}	1.3	5.00×10^{-4}	6.4	5.39×10^{-4}	14.7
293.15	8	0.6326	3.62×10^{-4}	3.94×10^{-4}	8.8	4.06×10^{-4}	12.2	4.41×10^{-4}	21.8
				NG5					
273.15	0.5	0.6672	1.16×10^{-3}	1.21×10^{-3}	4.3	1.25×10^{-3}	7.8	1.24×10^{-3}	6.9
278.15	0.5	0.6672	1.69×10^{-3}	1.75×10^{-3}	3.6	1.79×10^{-3}	5.9	1.82×10^{-3}	7.7
283.15	1.5	0.6672	8.36×10^{-4}	8.82×10^{-4}	5.5	8.78×10^{-4}	5.0	9.11×10^{-4}	9.0
288.15	1.5	0.6672	1.17×10^{-3}	1.21×10^{-3}	3.4	1.22×10^{-3}	4.3	1.25×10^{-3}	6.8
				NG6					
273.15	0.5	0.6395	1.22×10^{-3}	1.21×10^{-3}	0.8	1.25×10^{-3}	2.5	1.24×10^{-3}	1.6
278.15	0.5	0.6395	1.72×10^{-3}	1.75×10^{-3}	1.7	1.79×10^{-3}	4.1	1.82×10^{-3}	5.8
278.15	1.5	0.6395	6.03×10^{-4}	6.08×10^{-4}	0.8	6.25×10^{-4}	3.7	6.53×10^{-4}	8.3
283.15	1.5	0.6395	8.55×10^{-4}	8.82×10^{-4}	3.2	8.78×10^{-4}	2.7	9.11×10^{-4}	6.6
288.15	1.5	0.6395	1.16×10^{-3}	1.21×10^{-3}	4.3	1.22×10^{-3}	5.2	1.25×10^{-3}	7.8
288.15	6	0.6395	3.49×10^{-4}	3.35×10^{-4}	4.0	3.69×10^{-4}	5.7	4.02×10^{-4}	15.2
				NG7					
278.15	0.5	0.8107	1.76×10^{-3}	1.75×10^{-3}	0.6	1.79×10^{-3}	1.7	1.82×10^{-3}	3.4
				Synthetic Mixture Containing 96.94 mol % Methane and 3.06 mol % Ethane					
278.15	1.5	0.569	6.12×10^{-4}	6.08×10^{-4}	0.7	6.25×10^{-4}	2.1	6.53×10^{-4}	6.7
288.15	4	0.569	4.94×10^{-4}	4.84×10^{-4}	2.0	5.09×10^{-4}	3.0	5.44×10^{-4}	10.1
288.15	6	0.569	3.52×10^{-4}	3.35×10^{-4}	4.8	3.69×10^{-4}	4.8	4.02×10^{-4}	14.2
288.15	8	0.569	2.86×10^{-4}	2.75×10^{-4}	3.8	3.00×10^{-4}	4.9	3.31×10^{-4}	15.7
288.15	10	0.569	2.48×10^{-4}	2.41×10^{-4}	2.8	2.60×10^{-4}	4.8	2.88×10^{-4}	16.1

[a] AD% = |(experimental value − predicted value)/(experimental value)| × 100.

evaluate the performance of the ANN method, independent experimental data were used. Table 3 shows a comparison between the results of the above aforementioned method and experimental data on water content of various natural gases (NG) with the compositions given in Table 4. The predictions are also compared with the results of other predictive methods[2,18] in the literature. This table clearly shows that the effect of gas gravity (γ) can be ignored and the water content of sweet natural gases with low concentrations of heavy hydrocarbons is approximately equal to the water content of methane. A preliminary investigation of the predictions in Table 3 shows that the results of the ANN method (AAD = 3.2%) and the semiempirical method[2] (AAD = 5.1%) are in better agreement with the experimental data. The results of the Bukacek correlation[18] (AAD = 9.8%) show some deviations at low temperatures, typically at <288.15 K. It is interesting to compare the results of the ANN method for estimating the water content of nitrogen, because the water content of nitrogen is approximately equal to the water content of methane outside the hydrate phase boundary of methane.[2] Table 5 and Figure 5 show a comparison between the results of this method (AAD = 3.7%) and some selected experimental data from the literature. It can also be

Table 4. Composition of Different Natural Gases[a]

component	Composition (mol %)						
	gas gravity = 0.5654 (NG1)	gas gravity = 0.598 (NG2)	gas gravity = 0.628 (NG3)	gas gravity = 0.6326 (NG4)	gas gravity = 0.6672 (NG5)	gas gravity = 0.6395 (NG6)	gas gravity = 0.8107 (NG7)
helium	0.015	0.028		0.152	0.004	0.043	0.038
nitrogen	0.84	1.938	0.912	4.863	0.8	10.351	1.499
CO_2	0.109	0.851		0.167	1.732	1.291	25.124
methane	98.197	93.216	88.205	86.345	84.339	83.847	70.144
ethane	0.564	2.915	8.36	6.193	8.724	3.46	2.52
propane	0.189	0.715	1.763	1.55	3.286	0.657	0.394
i-butane	0.029	0.093	0.293	0.214	0.311	0.093	0.067
n-butane	0.038	0.135	0.441	0.314	0.584	0.126	0.074
C_5	0.014	0.058	0.027	0.13	0.163	0.067	0.054
C_{6+}	0.007	0.049		0.064	0.049	0.069	0.118

[a] From ref 12.

Table 5. Predicting the Water Content of Nitrogen Using the Validation Data Sets

			Using ANN		Using the Semiempirical Method[2]	
T (K)	*P* (MPa)	experimental water content (mol fraction)	predicted water content (mol fraction)	AD (%)	predicted water content (mol fraction)	AD (%)
			Maslennikova et al.[19]			
298.15	5	6.60×10^{-4}	7.49×10^{-4}	13.5	7.80×10^{-4}	18.2
298.15	7.5	5.00×10^{-4}	5.79×10^{-4}	15.8	5.70×10^{-4}	14.0
298.15	10	4.50×10^{-4}	4.69×10^{-4}	4.2	4.70×10^{-4}	4.4
323.15	5	2.75×10^{-3}	2.73×10^{-3}	0.7	2.90×10^{-3}	5.5
323.15	7.5	1.99×10^{-3}	2.11×10^{-3}	6.0	2.08×10^{-3}	4.5
323.15	10	1.58×10^{-3}	1.81×10^{-3}	14.6	1.68×10^{-3}	6.3
348.15	5	8.35×10^{-3}	8.55×10^{-3}	2.4	8.74×10^{-3}	4.7
348.15	7.5	6.05×10^{-3}	6.19×10^{-3}	2.3	6.19×10^{-3}	2.3
348.15	10	5.00×10^{-3}	4.97×10^{-3}	0.6	4.92×10^{-3}	1.6
373.15	5	2.15×10^{-2}	2.25×10^{-2}	4.7	2.23×10^{-2}	3.6
373.15	7.5	1.50×10^{-2}	1.60×10^{-2}	6.7	1.56×10^{-2}	3.7
373.15	10	1.17×10^{-2}	1.29×10^{-2}	10.3	1.22×10^{-2}	4.3
			Sidorov et al.[20]			
373.15	5.066	2.13×10^{-2}	2.23×10^{-2}	4.7	2.20×10^{-2}	3.3
373.15	10.133	1.17×10^{-2}	1.27×10^{-2}	8.5	1.21×10^{-2}	3.1
			Althaus[12]			
273.15	0.5	1.25×10^{-3}	1.21×10^{-3}	3.2	1.25×10^{-3}	0.0
273.15	1.5	4.30×10^{-4}	4.39×10^{-4}	2.1	4.40×10^{-4}	2.3
278.15	0.5	1.78×10^{-3}	1.80×10^{-3}	1.1	1.79×10^{-3}	0.6
278.15	1.5	6.00×10^{-4}	6.24×10^{-4}	4.0	6.30×10^{-4}	5.0
283.15	0.5	2.50×10^{-3}	2.55×10^{-3}	2.0	2.51×10^{-3}	0.4
283.15	1.5	8.40×10^{-4}	8.74×10^{-4}	4.0	8.80×10^{-4}	4.8
283.15	4	3.50×10^{-4}	3.50×10^{-4}	0.0	3.70×10^{-4}	5.7
283.15	6	2.50×10^{-4}	2.41×10^{-4}	3.6	2.70×10^{-4}	8.0
293.15	1.5	1.63×10^{-3}	1.64×10^{-3}	0.6	1.66×10^{-3}	1.8
293.15	4	6.50×10^{-4}	6.66×10^{-4}	2.5	6.90×10^{-4}	6.2
293.15	6	4.70×10^{-4}	4.73×10^{-4}	0.6	5.00×10^{-4}	6.4
293.15	8	3.80×10^{-4}	3.91×10^{-4}	2.9	4.10×10^{-4}	7.9
293.15	10	3.30×10^{-4}	3.30×10^{-4}	0.0	3.50×10^{-4}	6.1
			Rigby and Prausnitz[13]			
298.15	2.249	1.53×10^{-3}	1.53×10^{-3}	0.0	1.55×10^{-3}	1.4
298.15	3.09	1.15×10^{-3}	1.14×10^{-3}	0.9	1.16×10^{-3}	1.0
298.15	3.87	9.41×10^{-4}	9.29×10^{-4}	1.3	9.60×10^{-4}	2.0
323.15	2.109	6.26×10^{-3}	6.21×10^{-3}	0.8	6.26×10^{-3}	0.0
323.15	3.742	3.68×10^{-3}	3.51×10^{-3}	4.6	3.72×10^{-3}	1.1
323.15	5.982	2.42×10^{-3}	2.40×10^{-3}	0.8	2.50×10^{-3}	3.3
323.15	7.7	1.96×10^{-3}	2.08×10^{-3}	6.1	2.04×10^{-3}	4.3
348.15	4.221	1.01×10^{-2}	9.96×10^{-3}	1.4	1.02×10^{-2}	0.7
348.15	6.115	7.21×10^{-3}	7.23×10^{-3}	0.3	7.34×10^{-3}	1.8
348.15	8.972	5.23×10^{-3}	5.41×10^{-3}	3.4	5.35×10^{-3}	2.3
373.15	5.717	1.99×10^{-2}	2.00×10^{-2}	0.5	1.97×10^{-2}	1.0
373.15	7.948	1.50×10^{-2}	1.53×10^{-2}	2.0	1.48×10^{-2}	1.6
373.15	10.152	1.22×10^{-2}	1.27×10^{-2}	4.1	1.21×10^{-2}	1.1

concluded that the water content of sweet natural gases with various concentrations of nitrogen can be approximated by the water content of methane. For further evaluation of this method, the results are also compared with the results of the semiempirical approach (AAD = 3.9%).[2] The good agreement between the results demonstrates the reliability of both predictive tools. Sour natural gases will contain higher water contents than sweet natural gases. In Table 6, the water contents of some sour natural gases with low and intermediate concentrations of acid gases are predicted and compared with some experimental values. As can be seen, the ANN is capable of predicting the water content with acceptable accuracy (AAD = 9%) and the predictions are comparable to the results of the semiempirical method (AAD = 8.4%). Note that measuring the water content of gases, especially under low-temperature conditions, is very difficult, and an accuracy of 10% is generally acceptable.[1,2]

Table 6. Comparison between the Validation Data Sets on Water Content of Various Sour Gases (with Low and Intermediate Concentrations of Acid Gases) and Predictions from the ANN and Semiempirical[2] Methods

		Gas Composition (mol fraction)				Using ANN		Using the Semiempirical Approach[2]	
T (K)	P (MPa)	C_1	CO_2	H_2S	experimental water content (mol fraction)	predicted water content (mol fraction)	AD (%)	predicted water content (mol fraction)	AD (%)
					GPA Engineering Databook[21]				
311.15	13.8	0.89	0.11		8.08×10^{-4}	6.75×10^{-4}	16.5	7.63×10^{-4}	5.0
311.15	13.8	0.8	0.20		8.08×10^{-4}	6.75×10^{-4}	16.5	7.63×10^{-4}	5.6
327.15	10.3	0.92		0.08	2.21×10^{-3}	2.09×10^{-3}	5.4	1.98×10^{-3}	10.4
344.15	6.9	0.89	0.11		5.67×10^{-3}	5.54×10^{-3}	2.3	5.64×10^{-3}	0.5
344.15	6.9	0.8	0.20		5.59×10^{-3}	5.54×10^{-3}	0.9	5.64×10^{-3}	0.9
344.15	6.9	0.83		0.17	5.79×10^{-3}	5.54×10^{-3}	4.3	5.64×10^{-3}	2.6
344.15	9.43	0.725		0.275	4.90×10^{-3}	4.41×10^{-3}	10.0	4.39×10^{-3}	10.4
					Lukacs and Robinson[22]				
344.26	2.468	0.79		0.21	1.50×10^{-2}	1.42×10^{-2}	5.3	1.41×10^{-2}	6.0
344.26	4.212	0.81		0.19	9.30×10^{-3}	8.39×10^{-3}	9.8	8.67×10^{-3}	6.8
344.26	6.376	0.71		0.29	6.90×10^{-3}	5.91×10^{-3}	14.3	6.05×10^{-3}	12.3
344.26	6.962	0.83		0.17	6.16×10^{-3}	5.53×10^{-3}	10.2	5.62×10^{-3}	8.8
344.26	9.595	0.725		0.275	5.20×10^{-3}	4.37×10^{-3}	16.0	4.35×10^{-3}	16.4
344.26	9.616	0.84		0.16	4.75×10^{-3}	4.37×10^{-3}	8.0	4.34×10^{-3}	8.6
					Ng et al.[23]				
322.04	1.379	0.75	0.0625	0.1875	9.37×10^{-3}	9.02×10^{-3}	3.7	8.87×10^{-3}	5.3
322.04	1.379	0.75	0.1875	0.0625	8.74×10^{-3}	9.02×10^{-3}	3.2	8.87×10^{-3}	1.5
322.04	10.339	0.75	0.1875	0.0625	1.87×10^{-3}	1.69×10^{-3}	9.6	1.56×10^{-3}	16.6
322.04	10.339	0.75	0.0625	0.1875	1.81×10^{-3}	1.69×10^{-3}	6.6	1.56×10^{-3}	14.0
366.48	1.379	0.75	0.1875	0.0625	5.93×10^{-2}	5.38×10^{-2}	9.3	5.93×10^{-2}	0.0
366.48	1.379	0.75	0.0625	0.1875	5.97×10^{-2}	5.38×10^{-2}	9.9	5.93×10^{-2}	0.6
366.48	4.136	0.75	0.1875	0.0625	2.99×10^{-2}	2.15×10^{-2}	28.1	2.09×10^{-2}	30.2
366.48	10.339	0.75	0.1875	0.0625	1.12×10^{-2}	9.91×10^{-3}	11.5	9.45×10^{-3}	15.5
366.48	10.339	0.75	0.0625	0.1875	1.04×10^{-2}	9.91×10^{-3}	4.7	9.45×10^{-3}	9.6
366.48	10.339	0.75	0.1875	0.0625	1.01×10^{-2}	9.91×10^{-3}	1.9	9.45×10^{-3}	6.0

3.2. Estimating the Water Content of Natural Gases in Equilibrium with Gas Hydrates. Determination of the water content in a gas that is at equilibrium with gas hydrates is difficult, because of the very dilute concentration of water in the gaseous phase.[4] From a strictly thermodynamic standpoint, a gas phase (with dissolved water) can form gas hydrates without a free-water phase.[24] The question of the accumulation of a hydrate phase is a question of kinetics, which is dependent on the time necessary for hydrate nuclei to attain a critical size.[24] This time may be in excess of that available for laboratory study but may occur in processes that operate over extended periods of days, months, or years.[24] A literature survey reveals the availability of few sets of experimental data for water content of gases in equilibrium with hydrates and all other data represent metastable liquid water−gas equilibrium.[4] Therefore, few predictive methods for the water content of gases in equilibrium with hydrates have been reported in the literature, because these methods are generally based on experimental data.[4]

To evaluate the capability of the ANN for estimating the water content in equilibrium with gas hydrates, the experimental data for the water content of methane[25,26] and a gas mixture that

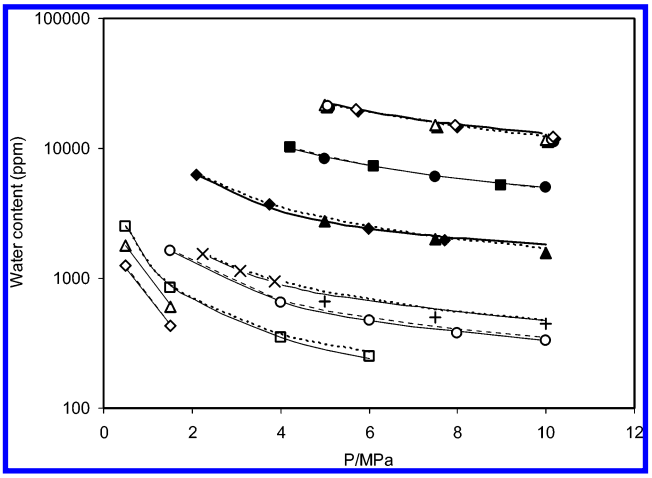

Figure 5. Experimental and predicted water content (given in terms of ppm (mol)) of nitrogen. Solid curves: Predictions of the ANN method; dashed curves: predictions of the semiempirical method.[2] Experimental data: (◇) 273.15 K,[12] (△) 278.15 K,[12] (□) 283.15 K,[12] (○) 293.15 K,[12] (×) 298.15 K,[13] (+) 298.15 K,[19] (◆) 323.15 K,[13] (▲) 323.15 K,[19] (■) 348.15 K,[13] (●) 348.15 K,[19] (◇ (shadowed)) 373.15 K,[13] (△ (shadowed)) 373.15 K,[19] and (○ (shadowed)) 373.15 K.[20]

Table 7. Number of Neurons, Hidden Layers, and Data Used in This Method for Estimating the Water Content in Equilibrium with Gas Hydrates

type	value/comment
layer 1	3 neurons
layer 2	6 neurons
layer 3	1 neuron
number of hidden layers	1
number of parameters	31
number of data used for training	48
type of function	exponential sigmoid

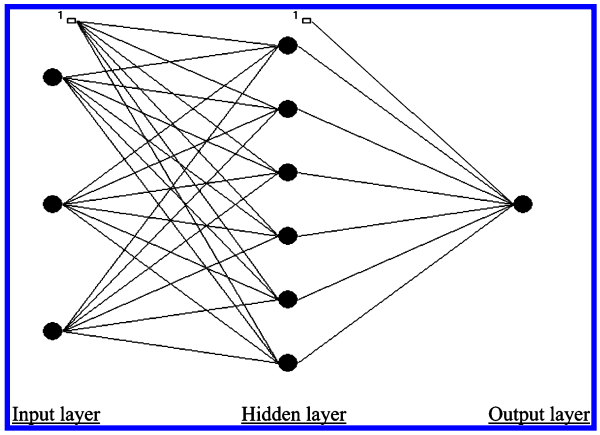

Figure 6. Architecture of the neural network method used to estimate the water content of natural gases in equilibrium with gas hydrates. Items marked "1" represent bias, whereas items marked by a solid circle (●) represent neurons. The output neuron is the logarithm of the water content, whereas the input neurons are the pressure (P), the inverse of temperature ($1/T$), and gas gravity (γ)).

Table 8. Experimental Data of the Learning Sets on Water Content of Gas in Equilibrium with Gas Hydrates Used for Developing This Method

reference	T_{min} (K)	T_{max} (K)	P_{min} (MPa)	P_{max} (MPa)	number of data points	AAD (%)	type of gas
Aoyagi et al.[25]	240	270	3.45	10.34	12	1.5	methane
Song et al.[26]	196	270	3.45	6.9	13	2.8	methane
Song and Kobayashi[27]	234.2	277.6	2.07	10.34	23	1.7	mixture of methane (94.69 mol %) and propane (5.31 mol %)

contains methane (94.69 mol %) and propane (5.31 mol %)[27] have been used for training. Figure 6 shows the architecture of the neural network method that was used; the details are reported in Table 7. As can be seen, three input neurons are used: pressure (P), the inverse of temperature ($1/T$), and gas gravity (γ). Note that the water content of gases in equilibrium with gas hydrates is a strong function of gas composition and, therefore, gas gravity. The number of hidden neurons was determined to be 6, according to the accuracy of the fit. Table 8 shows the data used in this study. A total of 48 data points have been examined. The temperature and pressure ranges are 196−277.6 K and up to 10.34 MPa, respectively, and the maximum percentage of absolute deviation (AD) is 5.6%. Figure 7 compares the experimental data reported in Table 8 with ANN results. To evaluate the performance of the ANN method, independent experimental data are necessary for validation. Unfortunately, more experimental data are not available in the literature to compare the predicted results with them. Therefore, the predictions are compared with the results of a previously recommended predictive technique, Kobayashi et al.'s method,[28] using the following example:

Example: Determine the water content of a gas whose gravity is 0.575 in equilibrium with a hydrate at 6.895 MPa and 260.04 K.

Answer: (from Kobayashi et al.[28]),
32.1 ppm (as reported in ref 24)
(from this work), 39.3 ppm

As can be seen, the water contents are in close agreement (a difference of 7.2 ppm is observed), which demonstrates the capability of this method for determining the water content of sweet natural gases in equilibrium with gas hydrates. This method is recommended for use to estimate the water content of sweet natural gases (with very low concentrations of heavy hydrocarbons) that are in equilibrium with gas hydrates at 234.2−277.6 K and at pressures up to 10.34 MPa, because the experimental data of methane (94.69 mol %) and propane (5.31 mol %)[27] at these ranges have been used to develop this method.

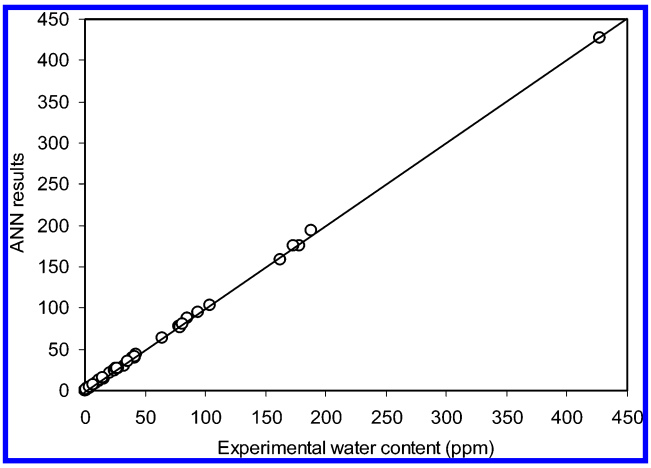

Figure 7. ANN results versus experimental data of the learning sets reported in Table 8.

The use of more-reliable water content data in the future can increase the accuracy of this method for estimating the water content of natural gases in equilibrium with gas hydrates.

4. Conclusions

Utilization of the neural network technique to estimate the water content of natural gases was investigated in the present work. The method utilized the updated experimental data on water content of gases, especially near and inside the hydrate region. It achieved acceptable accuracy when its predictions compared with independent experimental data and the results of other predictive techniques.

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Nomenclature

Abbreviations

ANN = artificial neural network
f = function
FNN = feed-forward (back-propagation) neural network
HC = hydrocarbons
NG = natural gas
RBF = radial basis function neural network
H = hydrate
I = ice
L = liquid
V = vapor

Parameters

AAD = average absolute deviation; AAD = $(1/N)\sum_{i=1}^{N}$ |[experimental value − predicted/calculated value]/[experimental value]| (%)
AD = absolute deviation; AD = |[experimental value − predicted/calculated value]/[experimental value]| (%)
err = residue vector; err = (experimental value) − (calculated value)
$\bar{H}$ = Hessian matrix
$\bar{I}$ = identity matrix
J = Jacobian matrix of the first derivative of the global error to weight
n = number of neurons in the hidden layer
N = number of experimental data/number of feed inputs in the Levenberg−Marquardt algorithm
P = pressure
Q = quadruple point
T = temperature
υ = weighted sum of input to the hidden neuron
w = weight
y = mole fraction in the gas phase
1 = bias

Greek Symbols

γ = gas gravity
μ = step values of Levenberg−Marquardt algorithm

Subscripts

HC = hydrocarbon
W = water
1 = lower quadruple point/index
2 = upper quadruple point/index

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