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Estimation of vapor–liquid equilibrium ratios of crude oil components: A comparative study

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HIGHLIGHTS

- We proposed a new simple correlation to predict the *K*-values of Iranian crude oil.
- The number of coefficients was reduced to 21 compared to 58 for Almehaideb.
- The capability of artificial neural network was also investigated.
- ANN had a relative reliable performance, compared to the other correlations.

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ABSTRACT

The present paper deals with the proposal of a new correlation for vapor–liquid equilibrium ratio of Iranian crude oil components, using multivariable regression techniques. The database for this study was collected from different Iranian reservoir oil fields extracted from differential liberation tests. They were measured at temperature range of 150–292 °F and pressures up to 4992 psia. Compared to the most published empirical correlations, the number of coefficients used in the new correlation was decreased from 58 for the Almehaideb correlation to 21. The second objective of this work was to estimate the equilibrium ratio by artificial neural network models. The absolute average relative error for the whole database was estimated 17.93% for artificial neural network, 33.98% for the new correlation, 28.98% for Almehaideb correlation, and 69.73% for Whitson & Torp correlation. Furthermore, the accuracy of the models for calculating the bubble points of ten samples compared with experimental values. The results shows the absolute average relative error of the artificial neural network to predict the saturation pressures was 5.38% compared to 14.50% for the new correlation and 8.01% for the Peng–Robinson equation of state without tuning. The results clearly depicts that over a range of experimental condition, the artificial neural network predictions indicate better agreement with experimental data than classic thermodynamic models.

1. Introduction

Modeling and design of several equipments for separating gas and liquids such as flash separators at the well head, distillation columns and even pipelines, are based on the phase's present being in vapor–liquid equilibrium (VLE). The criteria for thermodynamic equilibrium between vapor and liquid phases are: (1) equality of temperature in both phases, (2) equality of pressure in both phases, and (3) equality of fugacity of each component, in both phases. Equilibrium is most conveniently represented with an equilibrium vaporization ratio or *K*-value [1]. According to this study, *K*-value is described as the ratio of vapor-phase (y_i) to liquid phase (x_i) mole fraction of a constituent at given temperature and pressure [1]:

$$K_i = y_i/x_i \tag{1}$$

Numerous procedures have been developed to predict *K*-values; these include equations of state, combinations of equations of state with liquid theory or with tabular data, and corresponding states correlations. Depending on the system under study, any one of several approaches may be taken to determine *K*-values. Obviously, experimental measurement is the most desirable; however, it is expensive and time consuming. Alternatively, there are several graphical or numerical tools that can be used for determination of *K*-values. In general, the *K*-values for each component in a mixture are a function of the pressure, temperature and composition of the vapor and liquid phases.

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Nomenclature

a_1–a_3	new correlation parameters
%AARE	absolute average relative error percent
%ARE	absolute relative error percent
ANN	artificial neural network
b	bias (–)
BP	back propagation
DL	differential liberation
GDA	gradient descent with momentum
K	equilibrium ratio
LM	Levenberg–Marquardt
M_w	molecular weight (lbm/lb mol)
MSE	mean square error
MAE	mean absolute error
NN	neural network
P	pressure (psia)
Rs	gas to oil ratio (SCF/STB)
RP	resilient back propagation
SDEE	standard deviation error of the estimate
SCG	scaled conjugate gradient
T	temperature (°R)
VLE	vapor–liquid equilibrium
w	weight fraction (–)
x	mole fraction in liquid phase
y	mole fraction in gas phase
z	mole fraction in feed

Greek

α	new correlation parameter
γ	specific gravity
σ	standard deviation
ρ	density (lbm/ft^3)
ω	acentric factor

Subscripts and superscripts

b	bubble point
C_7^+	heptane plus fraction
c	critical point
g	gas
i, j, k	component
l, m, n, o, p	ANOVA parameters
L	liquid
r	reduced
STO	stock-tank oil
t	total

2. Literature review

Published works describe various approaches to predict a general correlation for *K*-values from experimental data, especially at high pressures. In 1968, Wilson suggested the following equation which is valid typically at relatively low pressures to estimate the equilibrium ratio [2]:

$$K_i = \frac{P_{ci}}{P_t} \exp\left[5.37(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right] \tag{2}$$

where P_{ci} is the critical pressure of component *i* (psia), P_t is the system pressure (psia), ω is the acentric factor, T_{ci} is the critical temperature of component *i* (°R) and *T* is the system temperature (°R). Wilson's equation basically uses Raoult's law, with the vapor pressure related to the critical properties. Whitson and Torp [3] modified Wilson's equation by incorporating the convergence pressure, P_k (psia), to obtain:

$$K_i = \left(\frac{P_{ci}}{P_k}\right)^{A-1}\left(\frac{P_{ci}}{P_t}\right) \exp\left[5.37(1+\omega_i)\left(1-\frac{T_{ci}}{T}\right)\right] \tag{3}$$

where

$$A = 1 - \left(\frac{P-14.7}{P_k-14.7}\right)^{0.6} \tag{4}$$

The concept of convergence pressure is based upon the observation that if a hydrocarbon mixture with certain composition is held at a constant temperature and increase the pressure, then the equilibrium ratios for all ~~its~~ components converge toward a value of unity at a certain pressure which is called the convergence pressure [4].

Ahmed [5] reviewed several methods to predict the convergence pressure. To calculate the convergence pressure, Rzasa [6] used the temperature and the product of the molecular weight and specific gravity of the heptane-plus fraction as correlating parameters to obtain

$$P_k = -2381.8542 + 46.341487(M_w\gamma)_{C7+} + \sum_{i=1}^{3} a_i\left(\frac{(M_w\gamma)_{C7+}}{T-460}\right)^i \tag{5}$$

where $(M_W)_{C7+}$ is the molecular weight of C_{7+}, $(\gamma)_{C7+}$ is the specific gravity of C_{7+}, a_1–a_3 are the correlation coefficients with the following values: $a_1 = 6124.3049$; $a_2 = -2753.2538$; $a_3 = 415.42049$. De Priester [7] also presented *K*-value charts for light hydrocarbons versus pressure and temperatures that are valid up to around 6000 psi or more. McWilliams [8] fitted these charts to the following polynomial equation:

$$LnK = \frac{a_{T1}}{T^2} + \frac{a_{T2}}{T} + a_{T3} + a_{P1}\ln P + \frac{a_{P2}}{P^2} + \frac{a_{P3}}{P} \tag{6}$$

where *T* is in °R and *P* is in psia. a_{T1}, a_{T2}, a_{T3}, a_{P1}, a_{P2} and a_{P3} are constants. McWilliams' equation is valid from 365.7 to 851.7 °R and from 14.69 to 870.7 psia.

Habiballah et al. [9] looked at some of the direct methods currently available in the literature for both high and low pressures, and commented that they generally lacked good accuracy. He used neural networks (NN) for prediction of *K*-values for light hydrocarbon mixtures. The results showed that NN method can successfully predict *K*-values for hydrocarbon mixtures. In 2003, Almehaideb et al. [10] improved *K*-value correlation at high pressures using the multivariable regression techniques. He used results of experimental PVT tests on 17 crude oil and gas samples obtained from a number of petroleum reservoirs in UAE. The form of developed equation is based on the polynomial form used in the McWilliams correlation, with additional term as a function of ω for the C_7^+ fraction. Moreover, an adjustment was considered for the effect of composition similar to the one suggested by Whitson and Torp. The developed equation is:

$$K_i = \left(\frac{P_{ci}}{P_k}\right)^{A-1}\left(\frac{P_{ci}}{P_t}\right) \exp[A \times K_i^*] \tag{7}$$

where

$$K_i^* = \frac{a_{T1}}{T^2} + \frac{a_{T2}}{T} + a_{T3} + a_{P1}\ln P + \frac{a_{P2}}{P^2} + \frac{a_{P3}}{P} + \frac{a_\omega}{\omega} \tag{8}$$

Recently, Fattah [11] presented a new model for predicting *K*-values with genetic programming; genetic programming is based on the Darwinian principle of reproduction and survival of the fittest and analogs of naturally occurring genetic operations.