VOL. 3, NO. 6, DECEMBER 2008 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences


www.arpnjournals.com

CRITICAL PROPERTIES OF HYDROCARBON MIXTURES BY ARTIFICIAL NEURAL NETWORK AND PENG-ROBINSON EOS

S. M. Hosseini[1], A. R. Fazlali[1] and G. R. Zahedi[2]
[1]Department of Chemical Engineering, Faculty of Engineering, Arak University, Arak, Iran
[2]Simulation and Artificial Intelligence Research Center, Department of Chemical Engineering, Razi University, Kermanshah, Iran
E-Mail: A-Fazlali@Araku.ac.ir

ABSTRACT

The calculation of critical properties of the petroleum fluids is important for practical and theoretical reasons. Experimental measurements of critical properties are time consuming, costly and very difficult. Therefore, they are often predicted using empirical correlations or thermodynamic models that can be calculated with moderate accuracy only up to pressures and temperatures near the critical region of the mixtures. In this model an Artificial Neural Networks (ANN) approach for the estimation of the critical properties of hydrocarbon mixtures is used. The typically collected experimental data after pre-scaling were used for the training and testing of the Artificial Neural Network. The results show very good capability of ANN to predict the data. Among the ANN's training, the Radial Basis Function (RBF) method gave the best prediction performance. The ANN model was also compared with the experimental data, and the data which was calculated based on the Peng-Robinson equation of state. The comparison confirmed the superiority of the ANN model.

Keywords: model, hydrocarbon mixture, properties, ANN, Peng-Robinson equation of state, radial basis function.

INTRODUCTION

Critical properties are essential in estimating thermodynamic and volumetric properties by the theorem of corresponding states. For example, in refinery, and chemical synthesis processes, involving the pressurized hydrocarbons gases, knowledge of the phase diagram is essential. Hydrocarbon mixtures are often supposed as systems which their phase behavior is easy to correlate and predict if their critical points are available. However, some questions, remains difficult to answer, especially about their high-pressure phase equilibria and critical point calculations. Experimental measurements of critical properties are time consuming, costly, and very difficult. Therefore, they are often predicted using empirical correlations and thermodynamic based models. The P-T diagram can be calculated with moderate accuracy only up to pressures and temperatures near the critical region of the mixture using equations of state. Some authors suggested methods for critical point calculations. Etter and Webster (Etter and Kay, 1961; Castier and Sandler, 1977; Jiang, and Prausnitz, 2000; Hoteit *et al.*, 2006) calculated the critical properties of normal paraffin mixtures. Castier and Sandler (Etter and Kay, 1961) calculated the critical properties with a modified Peng-Robinson equation of state and Wong-Sandler mixing rules. Jiang and Prausnitz (Castier and Sandler, 1977) performed the calculations of critical temperatures and pressures for hydrocarbon mixtures from an equation of state with renormalization-group theory corrections. Hoteit *et al.* (Shariati *et al*., 2008; Jiang, and Prausnitz, 2000) presented an efficient and robust algorithm for the calculation of gas-liquid critical point of multi-component petroleum fluids. Chaikunchuensakun and Tanthapanichakoon (Hoteit *et al.,* 2006) presented analytical partial derivative equations required for multi-component critical point calculation. In this work an Artificial Neural Networks (ANN) approach for the prediction of the critical properties of hydrocarbon mixtures has been proposed. Adoption of a black box approach, where models are obtained exclusively from experimental data, can provide other practical methods for modeling. These models provide a dynamic relationship between input and output variables and bypass underlying complexity inside the system. Statistical models based on the regression analysis are an example of such black box modeling (Zahedi *et al.*, 2008; Zahedi *et al.*, 2005; Valles, 2006; Osman and Al-Marhoun, 2002). Most of these common approaches rely on linear system identification models. The major processes found in the chemical engineering are unfortunately nonlinear processes, and previously mentioned approaches fail to respond regarding process nonlinearity. Recently, ANN has undergone numerous applications in chemical engineering ((Zahedi *et al.*, 2008; Zahedi *et al.*, 2005). ANN could perform better than regression models and is tolerant to the noise in data. ANNs can learn nonlinearities in the systems very well. Artificial neural networks are biological inspirations based on various characteristics of the brain functionality. They are composed of many simple elements called neurons that are interconnected by links that act like axons and dendrites of their biological counterparts and determine an empirical relationship between the inputs and outputs of a given system. Where the inputs of the system are the independent variables and the outputs are the dependent variables. A typical interconnected neural network is shown in Figure-1.

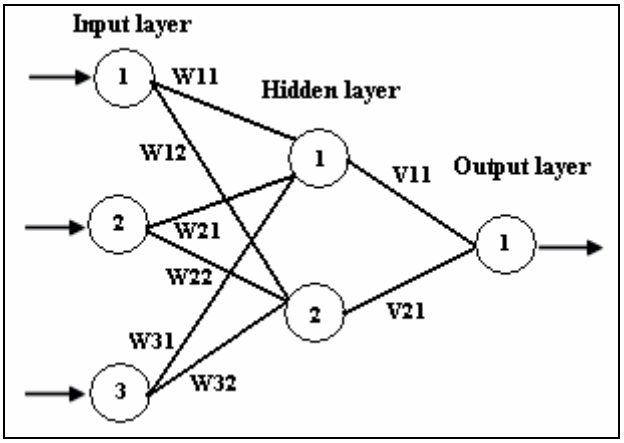

Figure-1. A typical interconnected neural network.

In this Figure an input layer, a central or hidden layer and an output layer can be seen. In a network each connecting line has an associated weight. Two important abilities of neural network (NN) are supplying fast answers to a problem and capability of generalizing answers, providing acceptable results for unknown samples. In this way, they should learn about the problem under study and this step is commonly named training process. One of the well-known topologies of neural networks for learning is the Multi-Layer Perceptron (MLP), which is used for classification and estimation problems. These Artificial neural networks are trained by adjusting the input weights (connection weights) by some algorithm so that the calculated outputs approximate the desired outputs (Zahedi *et al.*, 2008; Zahedi *et al.*, 2005). The output from a given neuron is calculated by applying a transfer function to a weighted summation of its input to give an output, which can serve as input to other neurons as follows:

$$p_j = f(\sum w_{ij} a_j) \quad (i = 0,\ldots, L) \qquad (1)$$

In this topology, there are L inputs, m hidden unit, and n output units. Where w_{ij} is weight going from input i to hidden unit j. using activation function f, and the output of neuron j is p_j.

Sigmoid activation functions are of common interest. Sigmoid tangential and other functions could be applied in ANN modeling (Zahedi *et al.*, 2008; Zahedi *et al.*, 2005 and Valles, 2006). ANN training is an optimization process in which an error function is minimized by adjusting the ANN weights. When an input training pattern is introduced to the ANN, it calculates an output. Output is compared with the real output provided by the user. This difference is used by the optimization technique to train the network. The typical performance function that is used for training neural networks is the Mean sum of Squares of the network Errors (MSE) which is given by Eq. (2)

$$MSE = (1/n) \sum (t_i - h_i)^2 \qquad (I = 1, n) \qquad (2)$$

Where h_i is the i^{th} real target and t_i is the network output corresponding to the j^{th} input. Thus, the training process is a path from input layer to output layer to calculate an output, obtaining error and a backward path to update the weights. The procedure goes on until MSE is minimized. During the training process, the train set error decreases since the ANN weights are adjusted according to the predicted errors from this set. The training process should stop when the tasking error reaches its minimum value. Besides MLP another class of networks has been known in recent years called Radial Basis Function (RBF) network. Like most feed forward networks, RBF networks have three layers, namely an input layer, the hidden layer with Gaussian activation function and output layer. The role of input layer is to distribute the inputs to each of hidden layer nodes. The weights on the links between the input layer and the hidden layer are set to unit and remain constant during training. Second layer or hidden layer performs a fixed nonlinear transformation which maps the input space onto a new space, the output layer then implements a linear combination on this new space. The network is solved by initially clustering the monitored process data, calculating the predictive error between experimental and network output. This continues until prediction error for all the data in which are used for training became minimum (Zahedi *et al.*, 2005 and 2008). Figure-2 shows a radial basis network with R inputs.

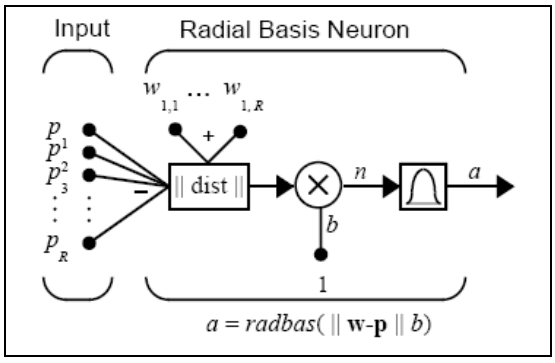

Figure-2. Radial basis network with R inputs.

Notice that the expression for the net work input of a radial basis (radbas) neuron is different from that of neurons in previous (i.e. MLP). Here the net work input to the radbas transfer function is the vector distance between its weight vector w and the input vector p, multiplied by the bias b. (The box in this case accepts the input vector p and the single row input weight matrix, and produces the dot product of the two.)

The transfer function for a radbas neuron is:

$$Radbas(n) = \exp(-n2) \qquad (3)$$

Figure-3 shows a plot of the radbas transfer function.

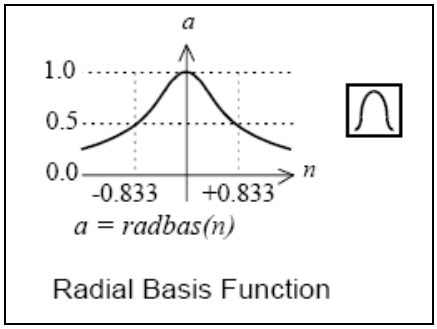

Figure-3. Plot of radbas transfer function.

The radbas function has a maximum of 1 when its input is 0. As the distance between w and p decreases, the output increases. Thus, a radbas neuron acts as a detector that produces 1 whenever the input p is identical to its weight vector p. The bias b allows the sensitivity of the radbas neuron to be adjusted (Matlab software's toolbox).

THE EXPERIMENTAL DATA SET

To build an ANN for predicting of the Critical properties of Hydrocarbon Mixtures, the experimental data provided. The data sets were collected from seventeen samples typically Hydrocarbon Mixtures. The specifications of Hydrocarbon Mixture samples are shown in Table-1 (Shariati *et al.*, 2008; Etter and Kay, 1961; Castier and Sandler, 1977; Jiang and Prausnitz, 2000; Hoteit *et al.*, 2006).

Table-1. Compositions of multi component mixtures.

Mixture No.	N2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}
Sample1	0	0	0.801	0	0	0.064	0	0.135
Sample 2	0	0	0.612	0	0	0.271	0	0.117
Sample 3	0	0	0.615	0	0	0.296	0	0.089
Sample 4	0	0	0.726	0	0.171	0	0	0.103
Sample 5	0	0	0.514	0	0.412	0	0	0.074
Sample 6	0.043	0.415	0	0.542	0	0	0	0
Sample 7	0.095	0.36	0	0.545	0	0	0	0
Sample 8	0.046	0.453	0	0.5005	0	0	0	0
Sample 9	0	0.833	0.130	0.035	0	0	0	0
Sample 10	0	0.800	0.039	0.161	0	0	0	0
Sample 11	0	0.4345	0.0835	0.4330	0	0	0	0
Sample 12	0	0.193	0.470	0	0.337	0	0	0
Sample 13	0	0.391	0.354	0	0.255	0	0	0
Sample 14	0	0.007	0.879	0	0.114	0	0	0
Sample 15	0	0.461	0.443	0	0	0.095	0	0
Sample 16	0	0.196	0.758	0	0	0.045	0	0
Sample 17	0	0	0.980	0.016	0.004	0	0	0

ANN applied for predicting the critical properties of hydrocarbon mixtures

Inputs of a network should be selected carefully if the best results are expected to be obtained. The input variables should reflect the underlying physics of the process to be analyzed.

Inputs for the network are compositions of multi component mixtures, acentric factor, critical properties for pure components, molecular weight of each component average molecular weight and binary interaction parameters between components; outputs are the critical temperature, pressure and volume. Various architectures of MLP and RBF are used to predict amount of Critical properties of Hydrocarbon Mixtures. Each type of input and output data were scaled by dividing to maximum amount of that variable for scaling purpose. Each ANN has been trained with (2/3) of data set and (1/3) of samples have been used for testing the predictions of ANN. In the first step, MLP architecture has been developed. The task was finding the optimum number of nodes in the hidden layer which provide good estimates of the outputs. The criterion for selection was MSE between net work output and training data. In the second step, RBF architecture was adopted.

Table-2 shows a comparison between the Performance of the RBF and the optimum MLP. As the

network trained with RBF architecture gives much better results for training sets than the optimal MLP, it was used for prediction of the critical Points of Hydrocarbon Mixtures.

Table-2. Comparison of performance of optimum MLP and RBF for testing the ANN.

Network type	MSE
Optimal MLP	1.042
RBF	4.73e-2

RESULTS OF MODELING WITH ANN

Figure-4 represents a sample comparison between predicted data by the ANN model and the experimental data which have not been used in training of the ANN (the test data). As shown in this figure, RBF method is more accurate than the other ANN structures. This is may cause of clustering in RBF that eliminates uncorrelated data from training process.

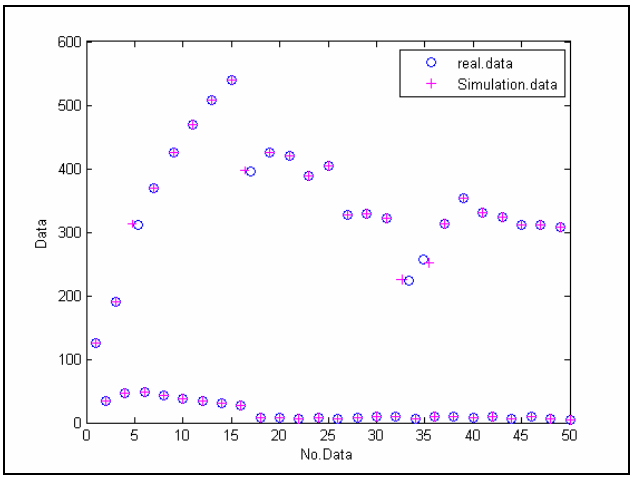

Figure-4. Comparison of the measured data and ANN results for RBF network class for critical point's hydrocarbon mixtures.

It is obvious from this Figure that the ANN provides results very close to process measurements. A scatter plot of measured experimental data against the ANN model predictions is shown in Figure-5. The predictions which match measured values should fall on the diagonal line. Almost all data lay on this line, which confirms the accuracy of the ANN model.

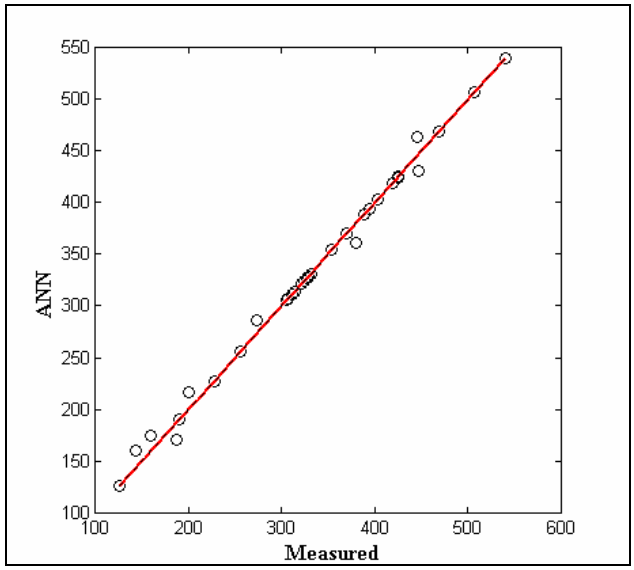

Figure-5. Plot of experimental data vs. predicted values by ANN model.

Thermodynamic model applied to predicting the critical properties of hydrocarbon mixtures

(Shariati *et al.*, 2008)

The formation of a new phase is generally preceded by some degree of super saturation. The bubble nucleation in a liquid at a pressure below its bubble point value can be inhibited to a large extent by expanding the liquid gradually, avoiding fluid agitation, and ensuring the lack of minute gas pockets in the liquid prior to the expansion. Such systems are Meta stable with an energy level which will be reduced by forming a new phase. The calculation is performed base on Peng-Robinson equation of state. This equation of state can be written as (Shariati *et al.*, 2008; Etter and Kay, 1961; Castier and Sandler, 1977; Jiang and Prausnitz, 2000; Hoteit *et al.*, 2006).

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 - 2bV - b^2} \quad (4)$$

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (5)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (6)$$

$$\alpha^{0.5} = 1 + (1 - T_r^{0.5})(0.37464 + 1.5422\omega - 0.26992\omega^2) \quad (7)$$

The mixture parameters a and b is as follow (2):

$$b = \sum y_i b_i \quad (8)$$

$$(a\alpha)_{ij} = (1 - k_{ij})\sqrt{(a\alpha)_i (a\alpha)_j} \quad (9)$$

$$a\alpha = \sum \sum y_i y_j (a\alpha)_{ij} \quad (10)$$

Where P (bar) is pressure , R is Universal gas constant, T (°K) is temperature , V (cm^3/mol) is Molar volume, *Tc* is Critical temperature, P_c is Critical pressure, T_r is Reduced temperature, ω is acentric factor, y_i is Mole fraction of

component i, b_i is Co volume of component i and k_{ij} is Binary interaction parameter.

Critical volume

For each mixture, first the metastable points are calculated using PR EOS. For this purpose, at each certain temperature, the volumes v_{min}, and v_{max} are obtained by solving the derivative $(\partial P / \partial V)T = 0$

At v_{min} the pressure has its minimum value in which the single liquid phase exist (at metastable condition) and at v_{max} the pressure has its maximum value in which the single vapor phase exist (at metastable condition). Then by extrapolating of the metastable volumes and solution of the following equations, the critical volume can be calculated (Shariati *et al.*, 2008; Etter and Kay, 1961; Castier and Sandler, 1977; Jiang, and Prausnitz, 2000; Hoteit *et al.*, 2006):

$$V_c = \exp(a_1 + b_1 V_{\min} + c_1 V_{\min}^2 + d_1 V_{\min}^3) \quad (11)$$

$$V_c = \exp(a_2 + b_2 V_{\max} + c_2 V_{\max}^2) \quad (12)$$

Critical temperature

For prediction of critical temperature, the metastable concepts, is used. For this method, the best equation for prediction of critical temperature as a function of metastable maximum volume is (Shariati *et al.*, 2008; Etter and Kay, 1961; Castier and Sandler, 1977; Jiang and Prausnitz, 2000; Hoteit *et al.*, 2006):

$$T_c = f(V_{\max}) \qquad T_c = \sqrt{a_3 + b_3 \ln V_{\max}} \quad (13)$$

By using of critical volume that calculated in the previous step, the critical temperature can be calculated.

Critical pressure

The critical pressure of a multi component mixture of hydrocarbons is calculated by the following equation (Shariati *et al.*, 2008; Etter and Kay, 1961; Castier and Sandler, 1977; Jiang and Prausnitz, 2000; Hoteit *et al.*, 2006):

$$P_{cmix} = P_{c,cal} + \sum \phi_i(y_i) \quad (14)$$

Where $P_{c,cal}$ is the critical pressure of the mixture that was calculated from extrapolating the P_{min} and P_{max} of the metastable points obtained for each isotherm till they cross each other. Also $\sum \phi_i(y_i)$ is the total excess critical pressure and is equal to the sum of the contributions of the excess critical pressure of the components, except the heaviest.

Comparison of experimental data with ANN and thermodynamic model results

Good performance of ANN is obvious when it is compared to other prediction models and experimental data. To check the performance of the ANN model, its estimations are compared with thermodynamic model base on PR EOS. Results carried out with the thermodynamic model were compared with ANN and also the experimental data which were not used in training of the ANN. Tables 3 and 4 also compares the error of both ANN and thermodynamic model. The prepared ANN model can be updated where new data are available. This task is applicable by retraining ANN using old ANN weights as initial weights for the new ANN. The ANN can be used to plan and control the operation of industrial oil. Optimization tasks can be carried out easily by the ANN model. The network will provide the outputs which represent the optimum condition for the prediction of critical properties of hydrocarbon mixtures.

Table-3. Comparison between the sample values of critical properties obtained from ANN models and thermodynamic model and the experimental data.

A sample of critical properties of hydrocarbon mixtures				
EXP	**ANN Model**	**Thermodynamic model**	**% Error for ANN model**	**% Error for Thermodynamic model**
T_c (°K) = 394.71	394.64	393.4617	0.0177	0.316
V_c (cm^3/mol) = 139.36	139.30	142.06	0.0430	2.36

Table-4. Comparison's performance of the ANN and thermodynamic model by the minimum square error.

Model Type	MSE
ANN model	0.0473
Thermodynamic model	3.8324

CONCLUSIONS

In this model, the ability of ANN in the modeling and prediction of the critical properties of hydrocarbon mixtures has been investigated. Specifically, the critical properties of hydrocarbon mixtures in the specific sample were modeled with RBF and MLP neural network architectures. By using RBF topology good agreement with experimental data was obtained. An important feature of the model is that, doesn't require any theoretical knowledge or human experience during the training process. So prior knowledge hasn't been used and the model has been trained based on the experimental data only. All unknown relationships have been represented with ANN, which can approximate instead of traditional

relationships. ANN models could be used instead of correlations in thermodynamic modeling by noting their application ranges. The ability of network could be extended to generate data in longer periods. In spite of this Limitation, ability of ANN in generation of data is excellent. In our approach minimum experimentation is necessary and this is a way to produce data with minimum time and cost.

Nomenclature

a	Attractive parameter of cubic EOS
a_i	Attractive parameter of component i
b	Co volume
b_i	Co volume of component i
calc	Calculated
EoS	Equation of state
Exp	Experimental
k_{ij}	Binary interaction parameter
P	Pressure
P_c	Critical pressure
PR	Peng-Robinson
R	Universal gas constant
T	Temperature
T_c	Critical temperature
T_r	Reduced temperature
V	Molar volume
V_c	Critical molar volume
V_{max}	Maximum metastable molar volume
V_{min}	Minimum metastable molar volume
y_i	Mole fraction of component *i*
ω	Acentric factor
α	Temperature-dependent parameter in Eos
ANN	Artificial neural network
MSE	Mean square error
RBF	Radial basis function
Wij	Weight
MLP	Multi layer percpetron
f	Activation function
t	Target value
h	Real value

REFERENCES

Zahedi G.R., Fazlali A.R., Hosseini S.M., Pazuki G.R. 2008. A Neural Network Approach for Prediction of Asphaltene precipitation and comparison it with Flory-Huggins model in crude oil. The 5th international congress on chemical engineering, Kish Island, Iran.

Shariati A., Mostafazadeh A. K., Bahramipibazari B.A. 2007. Calculation of Critical Points of Hydrocarbon Mixtures Using Metastability Concept. The first Iranian conference of thermodynamics, Isfahan University, Isfahan, Iran.

Zahedi G.R,.Jahanmiri A., Rahimpor M.R. 2005. A Neural Network Approach for Prediction of the CuO-ZnO-Al2O3 Catalyst Deactivation. International Journal of Chemical Reactor Engineering. Volume 3.

Vales H.R. 2006. A neural network method to predict activity coefficients for binary systems based on molecular functional group contribution. M.S. Thesis. University of PUERTO RICO.

Etter D.O. and Kay W.B. 1961. Critical properties of mixtures of normal paraffin hydrocarbons. Journal of Chemical and Engineering Data. Vol. 6, No. 3.

Castier M.and Sandler S.I. 1977. Critical points with the Wong-Sandler mixing rule- II. Calculations with a modified Peng-Robinson equation of state. Chemical Engineering Science. 52(20): 3579-3588.

Jiang J. and Prausnitz J.M. 2000. Critical temperatures and pressures for hydrocarbon mixtures from an equation of state with renormalization-group theory corrections. Fluid Phase Equilibria. p. 169.

Hoteit H., Santiso E. and Firoozabadi A. 2006. An efficient and robust algorithm for the calculation of gas-liquid critical point of multicomponent petroleum fluids. Fluid Phase Equilibria. p. 241.

Osman E.A., Al-MArhoun M.A. 2002. Using artificial neural networks to develop new PVT correlations for Saudi crude oils. 10th Abu Dhabi International Petroleum exhibition and conference. October.

Fazlali A.R, Hosseini .S.M and Khosrobeigi. E. 2007. A New thermodynamic modified Flory-Huggins model for prediction of asphaltene precipitation in crude oil. International Conference on mining, materials and petroleum engineering. Phuket, Thailand. May. pp. 10-12.

Ganguly S. 2003. Prediction of VLE data using radial basis function network. Computers and chemical engineering. 27: 1445-1454.

Sozen A., Arcakilioglu E., Ozalp M. 2004. Investigation of thermodynamic properties of refrigerant/absorbent couples using artificial neural networks. Chemical engineering and processing. 43: 1253-1264.

Suoqi Zhao, Zhiming Xu, Chunming Xu, Keng H. Chung. 2004. Feedstock characteristic index and critical properties of heavy crudes and petroleum residua. Journal of Petroleum Science and Engineering. p. 41.

Zhang Jianzhong, Zhao Suoqi, Wang Renan, Yang Guanghua. 1998. Prediction of critical properties of non-polar compounds, petroleum and coal-tar liquids. Fluid Phase Equilibria. p. 149.

Mohammad R. Riazi, Taher A. Al-Sahhaf, Mutlaq A. Al-Shammari. 1998. A generalized method for estimation of critical constants. Fluid Phase Equilibria. p. 147.