

Empirical Correlations and an Artificial Neural Network Approach to Estimate Saturated Vapor Pressure of Refrigerants

A.H. Meghdadi Isfahani^a, M. Reiszadeh^b, S. Yaghoubi Koupaye^c and M. Honarmand^{d,*}

^aYoung Researchers and Elite Club, Najafabad Branch, Islamic Azad University, Najafabad, Iran

^bChemical Engineering Department, Shahreza Branch, Islamic Azad University, Shahreza, Iran

^cDepartment of Mechanical Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran

^dDepartment of Mechanics, Tiran Branch, Islamic Azad University, Isfahan, Iran

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The examination of available vapor pressure data in the case of the methane, ethane, propane and butane halogenated refrigerants, allowed recommendations of standard equations for this property. In this study, three new models include a general correlation; a substance-dependent correlation and an artificial neural network (ANN) approach have been developed to estimate the saturated vapor pressure of refrigerants. With the presented approaches, vapor pressures have been calculated and compared with source data bank for 5600 data points of 28 refrigerants. The accuracies of new correlations and ANN have been compared with most commonly used correlations and the comparison indicates that all new models provide more accurate results than other literature correlations considered in this work.

Keywords: Vapor pressure, Correlation, Refrigerant, Approach, ANN

INTRODUCTION

Knowledge of the vapor pressure values of pure compounds such as refrigerants is essential for the design of process equipment especially in the field of refrigeration and air conditioning. Usually, vapor pressure data with a wide range of temperature are not accessible and also there is a lack of information about accurate measurements near the critical and triple points [1].

Because of the absence and limited range of saturated vapor pressure experimental data in the literature, some researchers have used different empirical models for vapor pressure to predict equation of state parameters [2-5].

Numerous models are reported in the literature for the vapor pressure prediction. The most commonly used model is a three-parameter Antoine type equation [6], which is valid only within a limited temperature range with

approximately high deviations. Although the Gomez-Thodos [7] and Lee-Kesler's equations [8] perform satisfactorily, they are generally failed to describe the critical region adequately.

One of the most efficient and accurate methods for calculating vapor pressure of pure substances, is computer-aided artificial neural network (ANN). Neural networks are information-processing patterns based on the biological nervous systems, such as the brain and process information [9]. Recently, ANN has been used to predict pressure-volume-temperature (PVT) properties of pure substances by Moghadasi *et al.* [10]. Rohani and coworkers [11] considered artificial neural network system and SAFT equation of state in obtaining vapor pressure and liquid density of pure alcohols. Lazzus [12] predicted solid vapor pressures of organic and inorganic compounds using ANN, and Gandhidasan *et al.* [13] estimated vapor pressures of aqueous desiccants for cooling applications.

This study represents a general correlation, a substance-dependent correlation, and an artificial neural network

*Corresponding author. E-mail: Mehرداد.honarmand@pa.iut.ac.ir

(ANN) approach based on liquid-vapor equilibrium data that accurately reproduces the vapor pressure behavior over a wide range of the liquid-vapor coexistence region. The source of vapor pressure data used in this study is the NIST Chemistry WebBook [14].

VAPOR PRESSURE CORRELATIONS

Lee-Kesler's Correlation

The Lee-Kesler's *correlation* [8] is one of the successful models to estimate the vapor pressure of pure substances using the three-parameter formulations.

$$\ln P_{vpr} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) \quad (1)$$

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6 \quad (2)$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 T_r^6 \quad (3)$$

where P_{vpr} is the reduced vapor pressure equal to P/P_c , and P_c is the critical pressure (pascal), ω is the acentric factor; T_r is the reduced temperature equal to T/T_c , where T_c is the critical temperature (K) of the fluid. Values for T_c and P_c can be found in the literature for many pure substances [15-18].

Ambrose-Walton Correlation

Ambrose and Walton [15] developed another representation of the Pitzer expansion with an additional term $f^{(2)}(T_r)$.

$$\ln P_{vpr} = f^{(0)}(T_r) + \omega f^{(1)}(T_r) + \omega^2 f^{(2)}(T_r) \quad (4)$$

$$f^{(0)} = \frac{-5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^5}{T_r} \quad (5)$$

$$f^{(1)} = \frac{-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^5}{T_r} \quad (6)$$

$$f^{(2)} = \frac{-0.64771\tau + 2.41539\tau^{1.5} - 4.26979\tau^{2.5} + 3.25259\tau^5}{T_r} \quad (7)$$

$$\omega = -\frac{\ln(P_c/1.01325) + f^{(0)}(T_{br})}{f^{(1)}(T_{br})} \quad (8)$$

where ω is the acentric factor, P_c is the critical pressure (bars) of the fluid, and $\tau = 1 - T_r$.

Riedel Corresponding States

Riedel [19] proposed a vapor pressure equation as follows:

$$\ln P_{vpr} = A + \frac{B}{T_r} + C \ln T_r + D T_r^6 \quad (9)$$

The T_r^6 term allows description of the inflection point of the vapor pressure curve in the high-pressure region. Parameters A , B , C and D are functions of T , T_c , T_b and P_c , which are presented in Supplementary data file (see Table 1 in Supplementary data file) for 28 refrigerants.

Wagner Equation

Wagner [20] used an elaborate statistical method to develop an equation for representing the vapor pressure behavior of nitrogen and argon over the entire temperature range for which experimental data were available. The resulting equation is:

$$\ln\left(\frac{P_{sat}}{P_c}\right) = \frac{A\tau + B\tau^{1.5} + C\tau^{2.5} + D\tau^5}{1 - \tau} \quad (10)$$

where $\tau = 1 - T/T_c$, P_c is the critical pressure, T_c is the critical temperature, and A , B , C and D are substance-dependent parameters presented in Supplementary data file (see Table 1 in Supplementary data file). Forero *et al.* in 2011 [21], determined Wagner equation parameters for 257 substances with low deviations.

Sanjari *et al.* Correlation

Sanjari *et al.* [22] proposed a vapor pressure correlation for refrigerants as follows:

$$\ln P_{vpr} = f^{(0)} + \omega f^{(1)} + \omega^2 f^{(2)} \quad (11)$$

$$f^{(0)}(T_r) = 6.834 - \frac{5.761}{T_r} + 0.907 \ln T_r - 1.169 T_r^{1.9} \quad (12)$$

Table 1. Average Absolute Deviation of the Values Obtained by Presented Models in Comparison with Literature Models

Substances	Lee-Kesler	Ambrose-Walton	Riedel	Wagner	Sanjari <i>et al.</i>	Model I	Model II	ANN
R11	0.94	1.14	1.42	1.64	1.41	1.13	0.52	0.21
R113	1.23	0.94	1.04	0.82	1.14	1.09	0.47	0.26
R114	1.51	1.31	1.56	1.40	0.89	1.14	0.40	0.38
R115	3.39	3.88	3.51	5.17	0.79	3.05	0.56	0.33
R116	2.52	0.40	2.53	3.08	1.11	0.88	0.69	0.25
R12	1.95	0.44	2.70	1.09	0.54	1.42	0.67	0.19
R123	1.44	0.60	1.17	0.34	0.85	1.06	0.45	0.26
R124	0.93	0.91	0.67	0.39	0.72	0.86	0.50	0.21
R125	1.15	1.53	0.93	1.10	1.24	1.75	0.58	0.23
R13	1.41	0.54	1.82	1.37	0.81	1.53	0.56	0.22
R134a	2.40	0.49	2.10	0.34	0.54	0.54	0.63	0.28
R141b	1.00	1.34	1.02	3.20	2.87	1.50	0.92	0.20
R142b	2.54	0.72	2.77	1.42	1.31	1.18	0.75	0.20
R143a	4.15	1.80	4.86	0.13	0.54	2.13	0.60	0.22
R152a	4.56	1.97	5.61	0.32	1.36	2.13	0.64	0.15
R21	0.91	1.92	0.72	6.97	1.11	2.49	2.04	0.26
R218	2.01	0.60	1.52	2.78	0.87	0.63	0.82	0.18
R22	1.06	1.22	1.64	1.45	0.57	0.92	0.71	0.25
R227ea	2.00	0.18	1.36	1.44	0.29	0.54	0.52	0.26
R23	4.46	1.79	5.73	0.27	1.16	2.46	0.75	0.28
R236ea	21.94	18.45	21.33	23.69	6.04	1.87	0.26	0.32
R236fa	1.93	0.50	1.02	2.24	3.26	0.58	1.12	0.23
R245ca	2.82	0.42	2.67	0.19	1.80	0.66	0.56	0.24
R245fa	0.67	2.65	1.35	0.21	5.60	2.30	0.70	0.29
R32	7.61	4.35	10.62	1.40	5.29	2.06	0.79	0.30
R41	11.04	7.38	17.08	1.57	2.79	2.80	1.36	0.38

$$f^{(1)}(T_r) = 5.320 - \frac{28.15}{T_r} - 58.04 \ln T_r + 23.57 T_r^{1.9} \quad (13)$$

$$f^{(2)}(T_r) = 18.20 + \frac{16.34}{T_r} + 65.70 \ln T_r - 35.97 T_r^{1.9} \quad (14)$$

ARTIFICIAL NEURAL NETWORK (ANN)

Neural networks (also referred to as connectionist systems) are a computational approach based on a large collection of neural units loosely modeling the way a biological brain solves problems with large clusters of biological neurons connected by axons. Each neural unit is connected with many others, and links can be enforcing or inhibitory in their effect on the activation state of the connected neural units. Each individual neural unit may have a summation function which combines the values of all its inputs together. There may be a threshold function or limiting function on each connection and on the unit itself such that it must surpass it before it can propagate to other neurons. These systems are self-learning and trained rather than explicitly programmed and excel in areas where the solution or feature detection is difficult to express in a traditional computer program [23].

Neural networks typically consist of multiple layers or a cube design, and the signal path traverses from front to back.

The sample for a three layer feed forward ANN is schematically presented in Fig. 1. An ANN includes some simple processing units as neurons. Each neuron of the ANN is connected to other neurons by direct connection links, which represents some information to solve the problem. Following equation can compute the output of a neuron:

$$O_j = f\left(\sum_{i=1}^n w_{ji}x_i + b_j\right) \quad (15)$$

where O_j = j th neurons output, f = transfer function or activation, w_{ji} = weight corresponding to i th synapse of j th neuron, b_j = bias of j th neuron, n = number of input signals to j th neuron and x_i = i th input signal to j th neuron [24,25]. Between all types of neural networks, the “Back

Propagation (BP)” method is the most universally used algorithm to estimate all thermodynamic properties of pure and mixture substances. Several back-propagation algorithms are including the Levenberg-Marguardt (LM), the Pola-Ribiere Conjugate Gradient (PCG), the Scaled Conjugate Gradient (SCG) and others. The LM, that similar to Gauss-Newton (GW) algorithm, is used in a back-propagation of deviation manner.

The large collection of samples needed to make an ANN with good quality. A set of data was collected from standard data bank [14]. Data source contains more than 5500 points of saturated pure refrigerants.

Number of neurons in hidden layer has been consistently varied to obtain a good predict of the trained data. Different number of neurons was considered to find the optimum number of nodes in the hidden layer, which provides good predict of the output. The scale for deviation was AAD% between output and training data. As shown in Fig. 2, architecture of ANN with 30 neurons has the least AAD% for data set with equals to 0.25%. Figure 3 shows the network structure with hidden layer include 30 neurons.

EMPIRICAL CORRELATIONS FOR VAPOR PRESSURE OF REFRIGERANTS

This work tried to find two rapid simple correlations to estimate vapor pressure of methane, ethane, propane and butane halogenated refrigerants based on vapor pressure data with high accuracy compared to literature correlations by using reduced temperature, critical pressure and acentric factor. There are some available data in source [14] to allow the comparison of equations for the vapor pressure of saturated refrigerants. After multiple regression analysis, two new equations were suggested as follows:

Model I: A General Substance-independent Equation

The new universal correlation is:

$$\ln P_{vpr} = f^{(0)} + \omega f^{(1)} \quad (16)$$

$$f^{(0)}(T_r) = 28.6854 - \frac{7.62604}{T_r} - 50.2698\sqrt{T_r} + 29.2219 T_r^{0.8} \quad (17)$$

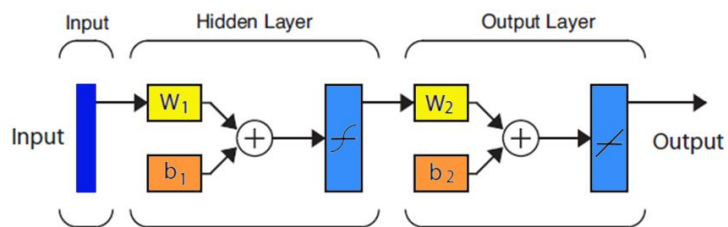


Fig. 1. The schematics structure of the three-layer feed forward neural network used in this study.

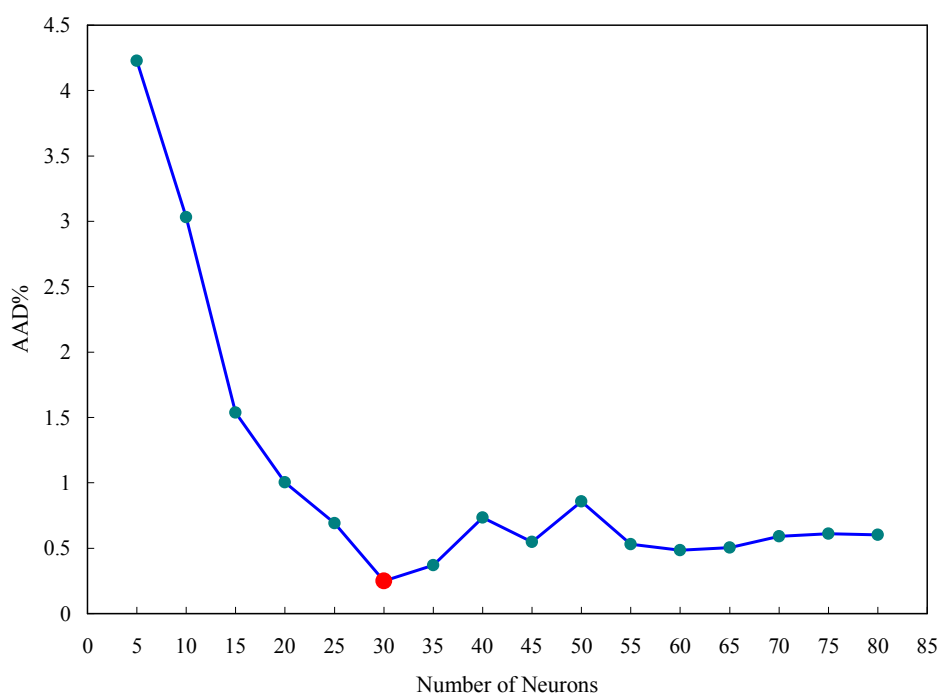


Fig. 2. Determining the optimum number of neurons.

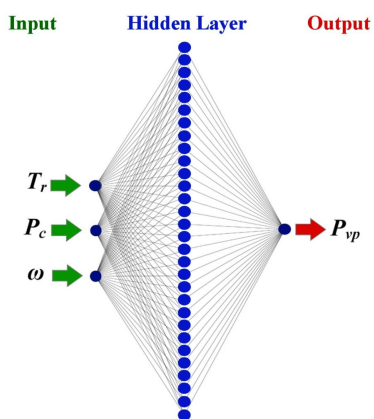


Fig. 3. Designed neural network structure.

Table 2. Statistical Parameters of this Study Compared with Literature Models

	AAD%	MSE%
Lee-Kesler	3.26	8.71
Ambros-Walton	2.21	7.51
Riedel	3.67	9.51
Wagner	2.51	8.17
Sanjari <i>et al.</i>	1.84	4.36
Model I	1.52	3.03
Model II	0.72	1.96
ANN	0.25	0.39

Table 3. Statistical Parameters of Considered Models for R14

	AAD%	MSE%
Lee-Kesler	2.14	4.13
Ambros-Walton	1.77	4.78
Riedel	2.71	4.63
Wagner	6.07	8.36
Sanjari <i>et al.</i>	1.80	6.71
Model I	0.94	3.07
Model II	0.75	1.89
ANN	0.21	0.32

$$f^{(1)}(T_r) = 66.3581 - \frac{15.4303}{T_r} - 97.6601\sqrt{T_r} + 46.6626 T_r^{0.8} \quad (18)$$

where P_{vpr} is the reduced vapor pressure, which is equal to P/P_c , $T_r = T/T_c$, is the reduced temperature, and ω is acentric factor.

Model II: An Accurate Substance-dependent Equation

In addition to the general method, a new substance-

dependent correlation is presented to predict saturated vapor pressure of refrigerants more accurate than other empirical models. The model is presented as follows:

$$\ln P_{vpr} = \sum_{i=1}^4 a_i T_r^{b_i} \quad (19)$$

where $b_1 = 0$, $b_2 = -1$, $b_3 = 0.1$ and $b_4 = 1.9$ are constant values for all refrigerants. a_1 to a_4 are constant substance-dependent parameters which their values for each substance

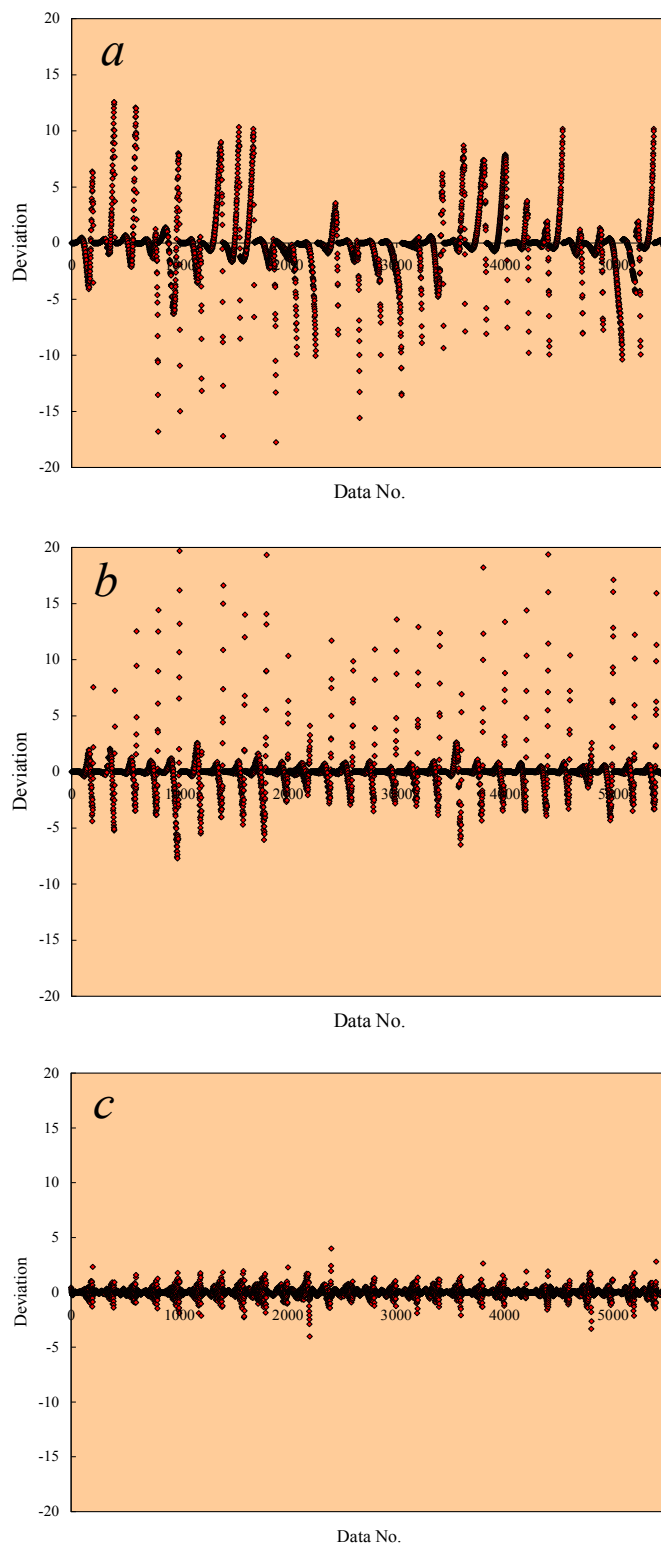


Fig. 4. Deviation of all data for 28 refrigerants calculated by; (a) general model; (b) substance-dependent model; (c) ANN.

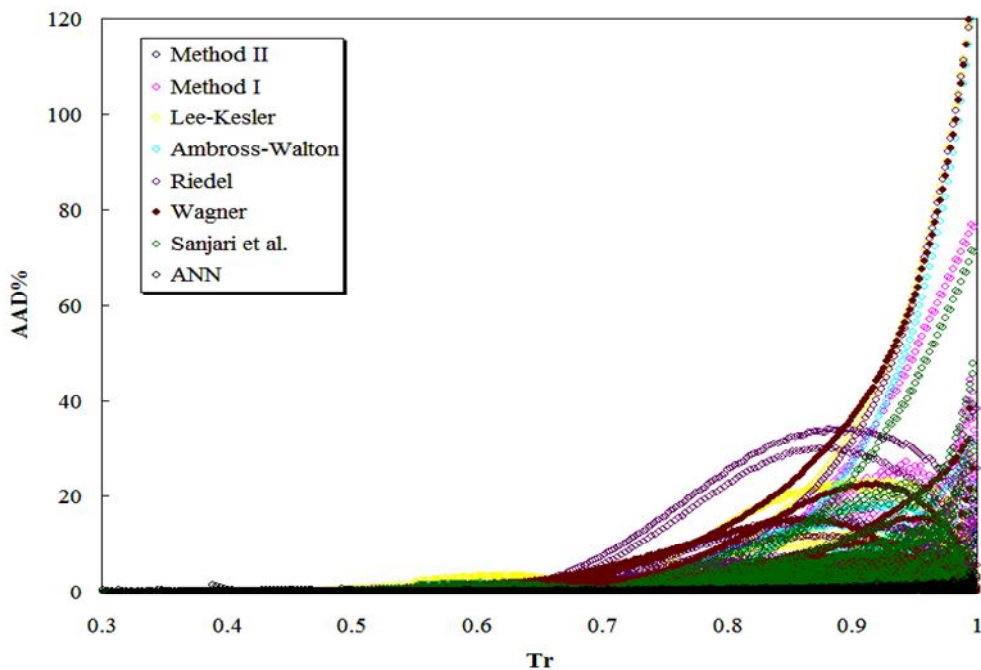


Fig. 5. AAD% against reduced temperature for all models.

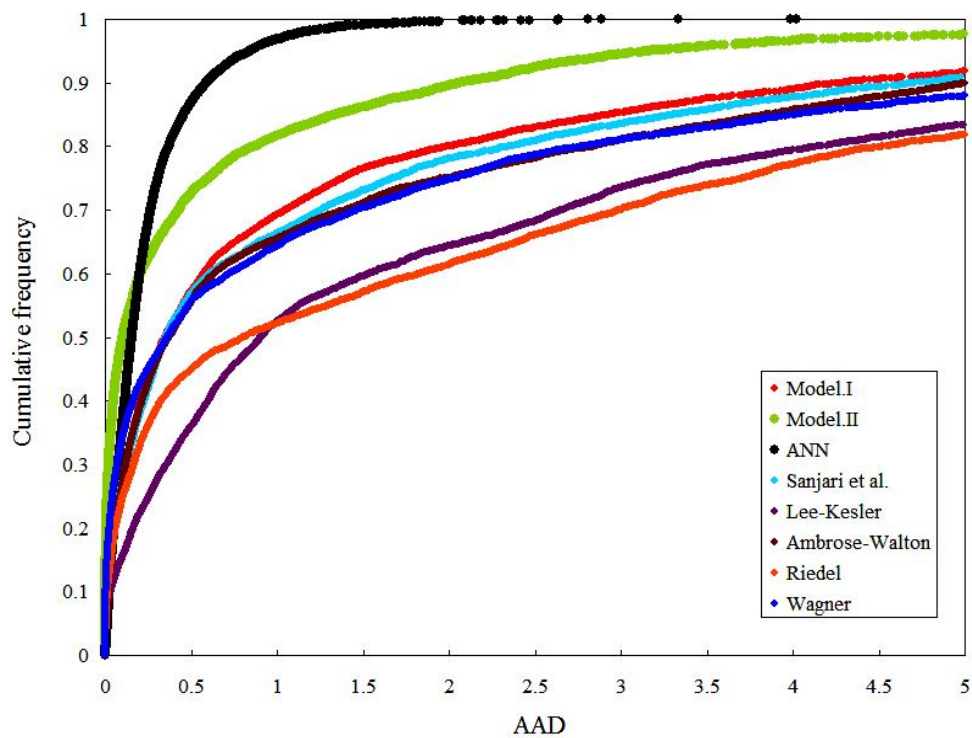


Fig. 6. AAD% of various methods in calculating vapor pressure as function of cumulative frequency.

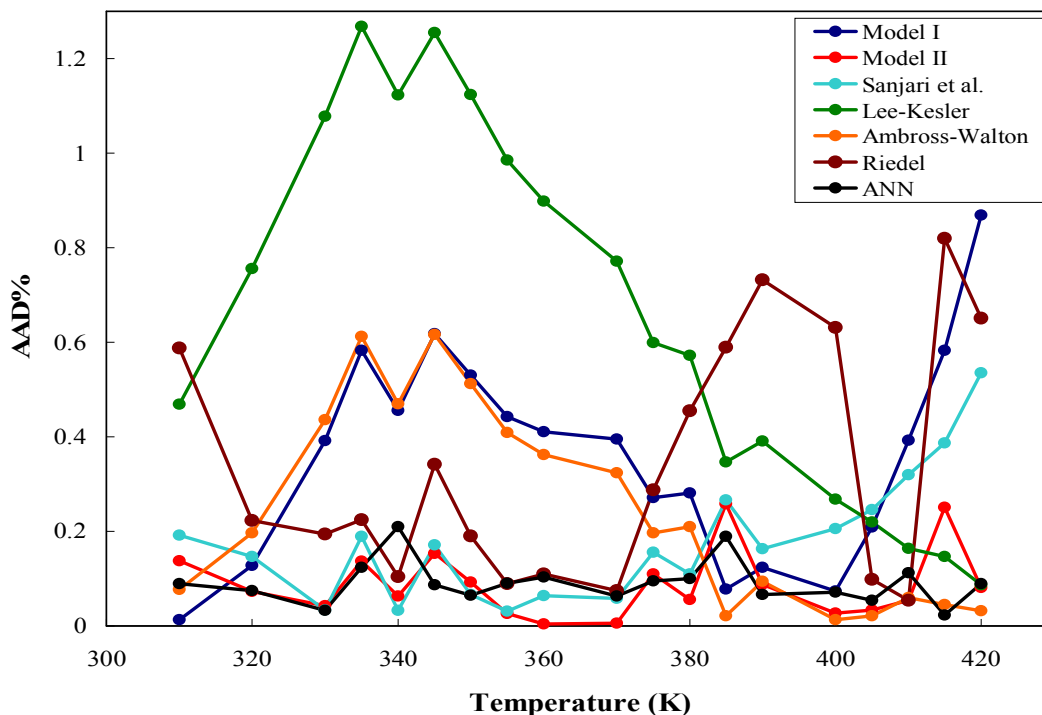


Fig. 7. Deviation of all models vs. temperature for R-1234ze(Z).

are presented in Supplementary data file (see Table 2 in Supplementary data file).

All tuned coefficients of two proposed correlations have been determined by using Marquardt-Levenberg algorithm which minimizes the sum of the squared differences between the observed and predicted values of dependent variables.

The temperature and pressure ranges, critical temperatures, critical pressures, and acentric factors required to set up the correlations have been reported in Supplementary data file (see Table 3 in Supplementary data file).

The new presented ANN structure and two correlations are obtained from investigating of a large number of vapor pressure data (NIST Chemistry WebBook) [14] for refrigerants.

RESULTS AND DISCUSSION

New predictive correlations are presented for vapor pressure calculation (Eqs. (16)-(18)) for general model and

Eq. (19) for substance-dependent model). Also we carried out calculations for all substances by using artificial neural network (ANN) approach. Vapor pressures for refrigerants from source data [14] have been calculated from these models and compared with five literature correlations.

The values of the vapor pressure, temperature, critical pressure, critical temperature, boiling point, and acentric factor, (for comparison with literature correlations) were taken from data bank [14].

To compare the accuracy of three presented models, deviations ($100 \times \{P_{source\ data} - P_{calculated}\}$) of each data point for all refrigerants is presented in Figs. 4a-c.

In Table 1 (rename Table numbers throughout the paper), AAD% of vapor pressure calculated from the proposed and literature models for each refrigerant with respect to the values given by data bank are presented.

AAD% can be calculated as follow:

$$AAD\% = \frac{\sum_{i=1}^N |P_{Source\ data} - P_{Calculated}|}{N} \times 100 \quad (20)$$

It showed that all three presented models have more accurate correlations compared to the literature correlations for all types of refrigerants considered in this study.

Table 2 presents the statistical parameters including average absolute deviation (AAD%), and mean square error (MSE%) for literature correlations and three new proposed models.

Figure 5 shows the deviation of all models for all substances versus reduced temperature. Figure 6 shows the cumulative frequency of the proposed models and different corresponding correlations versus average absolute deviations (AAD%). It shows the accuracy of each considered models in calculation of vapor pressure for all refrigerants. As illustrated in Fig. 5, three new proposed models are more accurate than other five commonly used correlations in vapor pressure calculation.

As indicated in Fig. 6, designated ANN has been successfully calculated 97% of all data with AAD less than 1. Model II, the second accurate model, and Model I, the third accurate model, have calculated 81% and 70% of data, respectively, with AAD of less than 1%.

Only 1.5% of calculations by Model I and 0.2% of values obtained by Model II were estimated with AAD% of more than 8%. Hence the superiority of this new correlation over the other literature models has been verified for all data existed in data bank.

To estimate the applicability of presented models for calculating vapor pressure of refrigerants, the statistical parameters of three proposed models and other mentioned correlations for 200 data points of R-14 [14] and 19 data of R-1234ze(Z) [26] are presented in Table 3 and Fig. 7. It should be noted that data points of R-14 and R-1234ze(Z) were not employed in regression analysis of the new proposed correlations.

The coefficients of Model II for R-14 are $a_1 = 79.836$, $a_2 = -9.822$, $a_3 = -72.110$, and $a_4 = 2.098$ and for R-1234ze(Z) are $a_1 = 154.4081$, $a_2 = 14.5079$, $a_3 = 143.7219$ and $a_4 = 3.8208$.

The results showed that Sanjari *et al.*'s equation is more accurate than literature correlations except this study three proposed models. ANN and Model II with lower deviation than considered correlations are best models with AAD% of 0.25 for R-14 and 0.081 for R-1234ze(Z), respectively.

CONCLUSIONS

For saturated vapor pressure of methane, ethane, propane and butane halogenated refrigerants, three predictive models including a general correlation, a substance-dependent correlation, and an artificial neural network (ANN) approach were recommended. These models were derived from NIST Chemistry WebBook. It is found that undesirable calculation deviations were obtained using Lee-Kesler and Riedel correlations. Sanjari *et al.*'s equation with constant parameters for each substance, generally gives good prediction than other previous models. New three predictive models were recommended to estimate vapor pressure of refrigerants more accurate than other commonly used correlations. To validate the proposed models, the vapor pressures of 27 refrigerants were examined and an overall AAD of 1.52% for the general equation (Model I), AAD of 0.72% for the substance-dependent equation (Model II), and AAD of 0.25% for the artificial neural network (ANN) approach was achieved. Also, to estimate the applicability of the new models, 200 data points of R14 and 19 data of R-1234ze(Z), which were not participate in regression analysis, were examined and the results showed again the superiority of all new presented models compared to other previous correlations.

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