

Predicting Vapor Pressure of Heavy Hydrocarbons from Molar Refraction and Its Applications to Petroleum Mixtures

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In this paper a generalized relation based on the corresponding states approach and use of molar refraction is proposed for the estimation of vapor pressure of pure hydrocarbons from C_1 to C_{100} . The hydrocarbons are divided into three groups of n -alkanes, n -alkylcyclohexanes, and n -alkylbenzenes from the paraffinic, naphthenic, and aromatic families. The method is also extended to undefined petroleum mixtures using bulk measurable properties, and unified methods are proposed for the calculation of input parameters from measurable properties of the mixture. The AAD for the proposed method for pure hydrocarbons (C_1 – C_{100}) and for temperature range of $T_r = 0.4$ to the critical point (ca. 91–968 K) for 1300 data points is 1.85% while from other available methods in the literature this error is about 24%. When evaluated against petroleum fractions the proposed method produces data slightly more accurate than the existing methods recommended specifically for petroleum mixtures. Application of the proposed method to vapor pressure of crude oil is also demonstrated.

Introduction and Background

Vapor pressure or saturation pressure is a thermodynamic property which is a characteristic of a substance, and it is a function of temperature. Vapor pressure data are needed for the design and operation of separation units (i.e., absorption, distillation, phase separator, etc.) in the chemical and petroleum industries. Vapor pressure is also needed in calculations related to safety and flammability range. In addition vapor pressure is needed for the calculation of the equilibrium ratio which is used for the phase equilibrium calculation of reservoir fluids in reservoir engineering calculations. Resources on conventional oils are limited and production of such oils is already in decline in some oil producing countries. In contrast resources for unconventional oils such as heavy and extra heavy oils or bitumen and tar oils are huge and some estimates put total world heavy oil reserves at about 10 trillion barrels.^{1,2} Therefore, the knowledge of vapor pressure of heavy and extra heavy oils is necessary in optimum utilization of these energy resources in coming decades.

At a given temperature (T) and at the corresponding vapor pressure (P^{vap}) the vapor and liquid phases are in equilibrium, and accordingly vapor pressure may be calculated through phase equilibrium calculations (equality of fugacity coefficients in vapor and liquid phases) through an equation of state. However, vapor pressure can be estimated more accurately and in a simpler way through methods specifically developed for this property based on available data. The simplest form of vapor pressure relation can be derived from Clausius–Clapeyron equation which yields a linear relation between $\ln P^{\text{vap}}$ and $1/T$. A more accurate version of this relation was suggested by Antoine in 1888 and is given as

$$\ln P^{\text{vap}} = A - \frac{B}{C + T} \quad (1)$$

where A , B , and C are constants specific for each compound. Constants for this equation for some pure hydrocarbons are

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given in the ASTM Manual 50.³ The above equation may be used for the pressure range of 0.02 to 2 bar although for some compounds the coefficients are given for a wider pressure range. There are some other expansions of the Clausius–Clapeyron equation such as

$$\ln P^{\text{vap}} = A + \frac{B}{T} + C \ln T + DT^2 + \frac{E}{T^2} \quad (2)$$

Constants A – E for some 300 hydrocarbon and nonhydrocarbon compounds are given in the API-Technical Data book.⁴ Another version of such equations has been used by DIPPR⁵ to represent vapor pressure of pure compounds and is given as

$$\ln P^{\text{vap}} = A + \frac{B}{T} + C \ln T + DT^E \quad (3)$$

In the above relation if $E = 6$, the equation reduces to the Riedel equation.³ These equations are applicable to pure compounds only in which data on the coefficients are available and usually show poor performance when applied outside the temperature range suggested for each compound. Coefficients for such relations are usually available for hydrocarbons up to C_{20} , although in some sources constants are given for heavier hydrocarbons as well. Any attempt to generalize these coefficients so they can be estimated for a system of unknown composition has been unsuccessful, and for this reason these methods cannot be referred as predictive methods.

One of the most successful generalized correlations for estimation of vapor pressure was proposed by Lee and Kesler⁶ in which reduced vapor pressure (P^{vap}/P_c) was correlated to reduced temperature (T/T_c) according to the corresponding states principles (CSP) using acentric factor (ω) as the third parameter, and it is given as

$$\begin{aligned} \ln P_r^{\text{vap}} = & 5.92714 - 6.09648T_r^{-1} - 1.28862 \ln T_r + \\ & 0.169347T_r^6 + \omega(15.2518 - 15.6875T_r^{-1} - 13.4721 \ln T_r + \\ & 0.43566T_r^6) \quad (4) \end{aligned}$$

In 1989 Ambrose and Walton added a third term to the right side of eq 4 and proposed the following correlation:⁷

$$T_r(\ln P_r^{\text{vap}}) = -5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^5 + \omega(-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^5) + \omega^2(-0.64771\tau + 2.41539\tau^{1.5} - 4.26979\tau^{2.5} + 3.25259\tau^5) \quad (5)$$

where $\tau = 1 - T_r$ and other parameters are the same as in eq 4. In the above equations, T_c , P_c , and ω should be estimated from the Lee–Kesler correlations when they are not available. Tsionopoulos et al.⁸ generalized eq 3 for hydrocarbons and coal liquid systems in the following form using acentric factor as a third parameter.

$$\ln P_r^{\text{vap}} = A - \frac{B}{T_r} - C \ln T_r + DT_r^6$$

$$A = 5.671485 + 12.439604\omega$$

$$B = 5.809839 + 12.755971\omega$$

$$C = 0.867513 + 9.654169\omega$$

$$D = 0.1383536 + 0.316367\omega \quad (6)$$

For undefined petroleum mixtures the method of Maxwell and Bonnell is recommended by the API Technical Data Book and it is given as⁴

$$\log P^{\text{vap}} = \frac{3000.538X - 6.761560}{43X - 0.987672}, \quad \text{for } X > 0.0022 \quad (P^{\text{vap}} < 2 \text{ mm Hg})$$

$$\log P^{\text{vap}} = \frac{2663.129X - 5.994296}{95.76X - 0.972546}, \quad \text{for } 0.0013 \leq X \leq 0.0022 \quad (2 \text{ mm Hg} \leq P^{\text{vap}} \leq 760 \text{ mm Hg})$$

$$\log P^{\text{vap}} = \frac{2770.085X - 6.412631}{36X - 0.989679}, \quad \text{for } X < 0.0013 \quad (P^{\text{vap}} > 760 \text{ mm Hg}) \quad (7)$$

where parameter X is defined as

$$X = \frac{T_b' - 0.00051606T_b'}{748.1 - 0.3861T_b'} T_b' = T_b - \Delta T_b, \quad \Delta T_b = 1.3889F(K_w - 12) \log \frac{P^{\text{vap}}}{760} F = 0, \text{ for } T_b < 366 \text{ K}$$

or when K_w is not available $F = -3.2985 + 0.009T_b$, for $367 \text{ K} \leq T_b \leq 478 \text{ K}$, $F = 1$, for $T_b > 478$ (8)

In this equation K_w is the Watson characterization factor ($K_w = T_b^{1/3}/SG$) where T_b is the average boiling point (in Rankine) and SG is the specific gravity of petroleum mixture. However, in eq 8 the unit of T_b is in Kelvin and the unit of P^{vap} is in mm Hg. Although this method is old, it still is a method which has wide industrial applications because of the availability of input parameters for undefined petroleum mixtures and its good accuracy for temperatures far from the critical temperature.

In any generalized correlation in which P_r^{vap} is related to T_r through the acentric factor (i.e., eqs 4, 5, or 6) one should realize that if the method is valid up to the critical point, as $T_r \rightarrow 1$, then we must have $P^{\text{vap}} \rightarrow P_c$ or $P_r^{\text{vap}} \rightarrow 1$. Also at the boiling point we should have $P^{\text{vap}} \rightarrow 1$ atm. While this condition is valid for eq 7, the Maxwell method is not recommended for the near critical region. Methods of Lee–Kesler and Ambrose are suitable for pure compounds up to the critical point but they show low performance for very heavy hydrocarbons. In addition these methods require T_c , P_c , and ω in which data are not available for heavy hydrocarbons and predictive methods give different estimates for hydrocarbons with a carbon number greater than 20.⁹ Most recently, Nji, et al.¹⁰ correlated vapor pressure of heavy hydrocarbons to molecular weight and specific

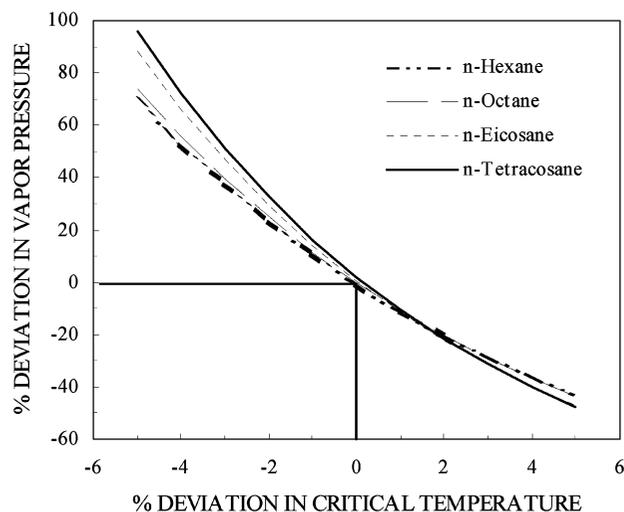


Figure 1. Impact of error in the critical temperature on calculation of vapor pressure for different hydrocarbons using eq 4.

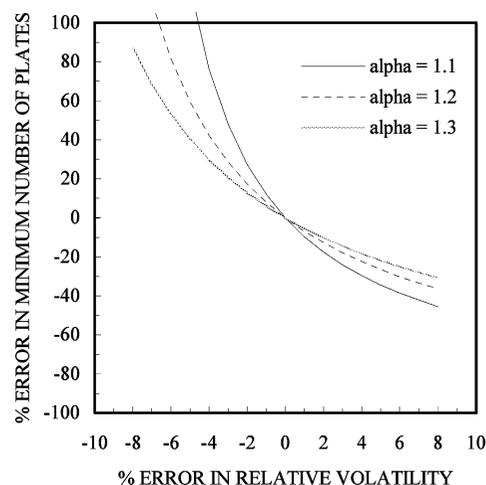


Figure 2. Impact of errors in the relative volatility on the calculation of number of trays in a distillation column.³

gravity using n -alkanes as the reference fluid. Their suggested method reproduced vapor pressure data and reported an average deviation of 17%.

Calculated vapor pressure through these methods is quite sensitive to the accuracy of input critical data. For example when the Lee–Kesler method (eq 4) is used to estimate vapor pressure of hydrocarbons, small errors on the critical temperature could significantly enlarge the errors on estimated vapor pressure as shown in Figure 1.³ These errors increase for heavier hydrocarbons in which experimental data on the critical constants is not available. Such errors can have significant consequences on the design of process equipment. For example in the calculation of number of theoretical trays through the Fenske equation where relative volatility is needed a small error on the relative volatility (which is directly proportional to vapor pressure) is translated into a much larger error on the calculated number of trays in a distillation column as shown in Figure 2. Another difficulty in using the above methods for calculation of vapor pressure of heavy oils and hydrocarbons is the lack of accurate data on the critical properties and acentric factor. From the above analysis it is clear that there is a need for the development of a predictive method for vapor pressure of various heavy hydrocarbons and extra heavy oils in which input

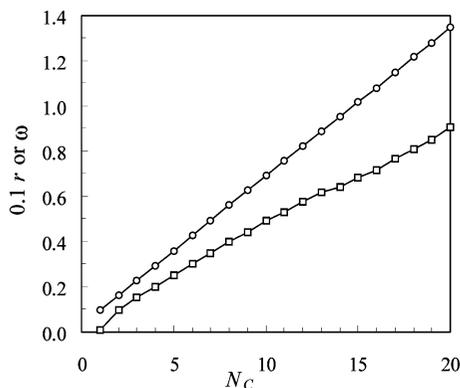


Figure 3. Variation of parameter r and ω with carbon number, N_C , for n -alkanes: \circ , $0.1r$; \square , ω .¹²

parameters can be directly measured or accurately estimated, and this is the main objective of this work.

Technical Development

In this work we attempt to develop a generalized relation based on the theory of corresponding states principles (CSP) for vapor pressure calculations using parameters that are easily available for heavy hydrocarbons and extra heavy oils. In conventional CSP methods (i.e., eqs 4 or 5) the acentric factor (ω) is used as a third parameter. This parameter is calculated from vapor pressure, critical temperature, and pressure and is not a measurable parameter. For heavy hydrocarbons such data are not available and various predictive methods lead to significant deviations for estimated values.³ In this work molar refraction is used as a third parameter in which it can be directly calculated from measurable properties.

Properties of fluids can be determined from the knowledge of intermolecular forces which exist between the molecules. For hydrocarbons systems London dispersion force is the main intermolecular force, and it is characterized by polarizability which is directly proportional to molar refraction, R_m :³

$$R_m = \frac{M(n^2 - 1)}{d(n^2 + 2)} \quad (9)$$

where M is the molecular weight, d is density, and n is the refractive index in which all are directly measurable. Density and refractive index are both functions of temperature and usually a reference temperature of 20 °C is used for d and n in the above relation. R_m is a parameter which represents molar volume of molecules in comparison with M/d which represents apparent molar volume. As methane is the simplest hydrocarbon it was chosen as a reference fluid for hydrocarbon systems, and parameter r is defined as

$$r = \frac{R_m}{[R_m]_{\text{CH}_4}} \quad (10)$$

The value of R_m for the reference fluid methane is 6.987 cm³/mol and r is a dimensionless factor. Methods of calculation of refractive index, n , are given in ref 11. Values of r for some hydrocarbons from C_1 to C_{40} are given in ASTM MNL50.³ The main advantage of r versus ω is that the variation of r with carbon number is linear, while this is not the case for ω as shown in Figure 3.¹²

To develop a new CSP relation for vapor pressure of heavy hydrocarbons, values of critical temperature and pressure are also required. Predictive methods which are specifically pro-

posed for heavy hydrocarbons are given in Appendix A.⁹ These relations are consistent with vapor pressure requirements in which for very heavy hydrocarbons as $P_c \rightarrow 1$ atm, $T_c \rightarrow T_b$, and we use them as standard methods for the calculation of parameters needed for our method. On the basis of the data on vapor pressure of conventional hydrocarbon compounds (C_1 to C_{20}) the following simple relation based on the CSP was found to be suitable for pure hydrocarbons:

$$\ln P_r^{\text{vap}} = (a_1 + a_2r + a_3r^2) + (b_1 + b_2r + b_3r^2)T_r^{-2} + (c_1 + c_2r)T_r \quad (11)$$

where P_r^{vap} is the reduced vapor pressure and T_r is the reduced temperature and r is calculated through eq 10. The input parameters for this equation are T_c , P_c , d_{20} , n_{20} , and M which all can be calculated from methods in Appendix A for heavy hydrocarbons based on the carbon number or molecular weight of the compound.

In the development of eq 11, at first for the simplest fluid of methane with $r = 1$, the relation between $\ln P_r^{\text{vap}}$ and T_r was found to be as $\ln P_r^{\text{vap}} = a + bT_r^{-2} + cT_r$, and then coefficients a , b , and c were related to r to generalize the equation for other compounds. Furthermore there was an attempt to keep the equation in a simple form to have greater extrapolation capability when applied to heavier compounds. It should be noted that the input parameters needed for the use of eq 11 (T_c , P_c , and r) must be calculated from the methods given in Appendix A.

Data on the vapor pressure of pure hydrocarbons was taken from Dykyj, et al.¹³ in which vapor pressure data for hydrocarbons from C_1 to C_{100} are given. Coefficients a , b , and c in eq 11 were determined for three cases: C_1 – C_{50} , C_{50} – C_{100} , and C_1 – C_{100} ranges for three hydrocarbon groups of n -alkanes, n -alkylcyclohexanes, and n -alkylbenzenes in which full data were available on vapor pressure. In addition these are three key hydrocarbon families for the use of pseudocomponent methods for petroleum mixtures.³ Constants a , b , and c for use in eq 11 are given in Table 1 as determined from this database for pure homologous hydrocarbons.

Evaluation of Proposed Method for Pure Hydrocarbons

Tables 2 and 3 show the overall results and detailed comparison with other methods for 1300 data points in terms of AAD% and AD, respectively. In use of Lee–Kesler and Ambrose methods the critical constants and acentric factor were determined from the Lee–Kesler correlations which have been recommended when eq 4 and eq 5 are used.³

For n -alkanes, coefficients no. 1 are used to predict vapor pressure from methane (C_1) to n -pentacontane (C_{50}). While coefficients no. 2 are used from n -hentapentacontane (C_{51}) to n -heptane (C_{100}). Also, coefficients no. 3 can be used directly from methane to C_{100} , although there is a moderate increase in the AAD% error. For example, coefficients no. 1 and no. 2 give errors of 1.8% and 1.3%, respectively, while coefficients no. 3 give 3.1% error. For very heavy hydrocarbons the numerical values of vapor pressure data are so small that small deviations are reflected into much larger relative errors in terms of AAD% (Table 2), whereas when errors are calculated in terms of absolute deviation (AD), the errors even reduce further for heavier hydrocarbons as shown in Table 3. Other methods such as Lee–Kesler, Riedel, and Ambrose give errors (AAD%) of 4.0%, 9.3%, and 3.5%, respectively, based on data from n - C_1 to n - C_{50} , while from n - C_{51} to n - C_{100} these methods give errors of 31.0%, 31.5%, and 32.9%, respectively. For other hydrocarbon groups such as n -alkylcyclohexanes and n -alkylbenzenes

Table 1. Coefficients for Equation 11 for Vapor Pressure Prediction and Corresponding Applicable Ranges

no.	C_n range	overall range ^a		constants							
		T (K)	T_r	a_1	a_2	a_3	b_1	b_2	b_3	c_1	c_2
<i>n</i> -Paraffins											
1	C_1 – C_{50}	91–858	$0.4-1^b$	-3.0337	0.3265	-0.0018060	-1.0097	-0.20560	0.0017020	4.0519	-0.12160
2	C_{51} – C_{100}	560–945	$0.6-1^b$	0.9948	0.1581	-0.0006864	-2.5795	-0.12750	0.0008085	1.5701	-0.03715
3	C_1 – C_{100}	91–945	$0.4-1^b$	-3.0123	0.2895	-0.0014210	-1.0468	-0.19190	0.0014120	4.0572	-0.09815
<i>n</i> -Naphthenes, <i>n</i> -Alkylcyclohexanes											
4	C_6 – C_{50}	262–856	$0.5-1^c$	-4.0105	0.3526	-0.0025650	-0.6714	-0.21920	0.0024750	4.7299	-0.13560
5	C_{51} – C_{89}	562–968	$0.6-0.9$	1.2228	0.1323	-0.0007327	-2.8616	-0.09522	0.0006825	1.3859	-0.03081
6	C_6 – C_{89}	262–968	$0.5-1^c$	-3.8151	0.3077	-0.0019230	-0.8466	-0.18830	0.0016790	4.5399	-0.10710
<i>n</i> -Aromatics, <i>n</i> -Alkylbenzenes											
7	C_6 – C_{50}	279–856	$0.5-1^d$	-2.8541	0.3111	-0.0015670	-0.8979	-0.20640	0.0016600	3.8380	-0.12690
8	C_{51} – C_{90}	562–968	$0.6-1^d$	1.4566	0.1361	-0.0007567	-2.4761	-0.13090	0.0009164	1.0438	-0.02672
9	C_6 – C_{90}	279–968	$0.5-1^d$	-2.262	0.2587	-0.0015010	-1.0222	-0.19330	0.0015320	3.2853	-0.08027

^a Based on the minimum and maximum T_r of all compounds in the group. Approximate ranges are given as follows: ^b For C_{11} – C_{17} and C_{21} – C_{27} $T_r \leq 0.8$; for C_{18} – C_{20} , C_{28} – C_{56} , C_{58} – C_{59} and C_{81} – C_{83} $T_r \leq 0.9$. ^c For C_8 , C_{14} and C_{26} $T_r \leq 0.6$; for C_9 – C_{13} , C_{15} – C_{25} and C_{27} – C_{35} $T_r \leq 0.8$; for C_{36} – C_{89} $T_r \leq 0.9$. ^d For C_{10} – C_{20} and C_{23} – C_{27} $T_r \leq 0.8$; for C_{21} , C_{22} and C_{29} – C_{62} $T_r \leq 0.9$.

Table 2. Evaluation of Various Methods for Estimation of Vapor Pressure of Different Hydrocarbon Groups in Relative Errors

C_n range	%AAD				%MAD				no. of data points ^a
	new method	LK	Riedel	Ambrose	new method	LK	Riedel	Ambrose	
<i>n</i> -Paraffins									
C_1 – C_{50}	1.83	4.03	9.28	3.48	38.7 (C ₄₂) ^b	40.8 (C ₄₂)	105.2 (C ₂₁)	35.1 (C ₄₂)	250
C_{51} – C_{100}	1.33	31.03	31.50	32.90	12.3 (C ₈₆)	87.1 (C ₁₀₀)	84.9 (C ₁₀₀)	89.2 (C ₁₀₀)	210
C_1 – C_{100}	3.14	16.36	19.42	16.91	39.2 (C ₄₂)	87.1 (C ₁₀₀)	105.2 (C ₂₁)	89.2 (C ₁₀₀)	460
<i>n</i> -Naphthenes, <i>n</i> -Alkylcyclohexanes									
C_6 – C_{50}	3.42	17.86	16.51	19.07	34.0 (C ₆)	55.3 (C ₅₀)	56.3 (C ₁₀)	61.3 (C ₅₀)	225
C_{51} – C_{89}	1.09	55.82	56.25	57.09	3.8 (C ₈₉)	94.2 (C ₈₉)	92.9 (C ₈₉)	95.5 (C ₈₉)	195
C_6 – C_{89}	7.24	35.48	34.96	36.72	42.7 (C ₈₉)	94.2 (C ₈₉)	92.9 (C ₈₉)	95.5 (C ₈₉)	420
<i>n</i> -Aromatics <i>n</i> -Alkylbenzenes									
C_6 – C_{50}	2.07	13.82	19.14	11.62	20.5 (C ₆)	50.8 (C ₅₀)	101.4 (C ₃₆)	36.7 (C ₅₀)	220
C_{51} – C_{90}	1.12	31.66	32.84	28.08	3.9 (C ₇₈)	60.0 (C ₈₉)	84.5 (C ₅₁)	53.5 (C ₈₉)	200
C_6 – C_{90}	3.24	22.32	25.66	19.46	18.4 (C ₉)	60.0 (C ₈₉)	101.4 (C ₃₆)	53.5 (C ₈₉)	420
Overall (All Groups) ^c									
C_1 – C_{100}	1.85	24.46	26.46	24.13	42.7 (C ₈₉)	94.2 (C ₈₉)	105.2 (C ₂₁)	95.5 (C ₈₉)	1300

^a Vapor pressure data reference: Dykyj et al.¹³ ^b The carbon number which have the maximum absolute deviation. ^c Based on the first two divided ranges of each group. Lee–Kesler, Ambrose, and Riedel methods are given as eqs 4, 5 and 6, respectively. %AAD is the average absolute % deviation and %MAD is the maximum absolute % deviation.

almost the similar results as *n*-alkanes are observed. The proposed method gives errors of 3.4% and 1.1% for *n*-alkylcyclohexanes using coefficients no. 4 and no. 5, respectively, while for *n*-alkylbenzenes it gives 2.1% and 1.1%, using coefficients no. 7 and no. 8. In Tables 2 and 3 maximum errors are also reported for each method along with the exact carbon number at which the maximum error is observed.

To show evaluation of the proposed method over the entire range of temperature, vapor pressure data and calculated values for *n*-C₁₀₀ (paraffin family), *n*-nonacosylcyclohexane C₃₅, and *n*-trioctacetyl-cyclohexane C₈₉ (naphthenic family) are shown in Figures 4, 5, and 6, respectively. Figure 7 panels a and b show evaluation of various methods for vapor pressure of *n*-alkanes from C₁ to C₁₀₀ at a reduced temperature of 0.8. In Figure 7b vapor pressure is shown on a log-scale for better evaluation of the vapor pressure of heavy hydrocarbons which in Figure 7a is not distinguishable. Evaluation of the proposed method for extra heavy *n*-alkanes at $T_r = 0.8$ is shown in Figure 8. Evaluation of various predictive methods for vapor pressure of aromatic hydrocarbons from C₆ to C₉₀ is shown in Figures 9 and 10. As shown in Figures 7–10, the proposed method shows

significant improvement over the existing methods especially for heavy and extra heavy hydrocarbons.

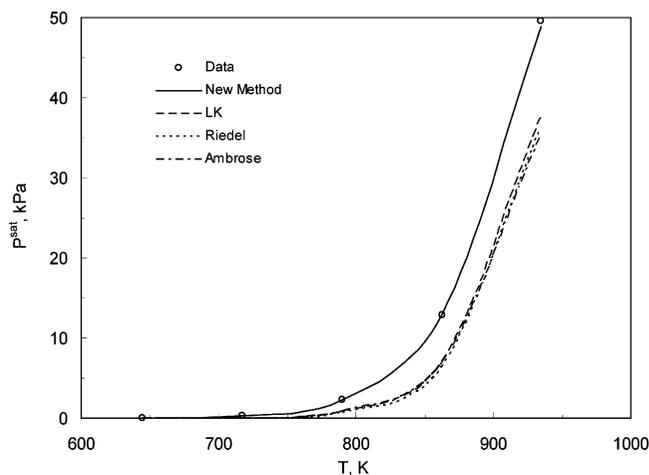
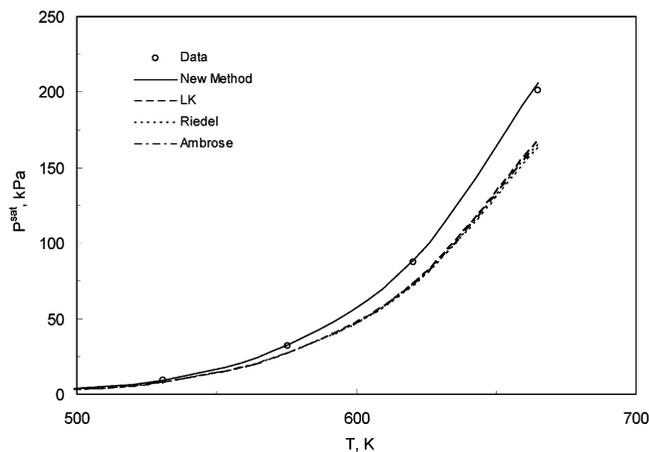
Application of the Proposed Method to Near and at the Critical Point

Theoretically a predictive method for vapor pressure of pure compounds could be valid from the triple point to its critical point. At the critical temperature ($T_r = 1$) the true vapor pressure is equal to the critical pressure, that is $P_r^{\text{vap}} = 1$ or $\ln P_r^{\text{vap}} = 0$. This condition has been imposed in both the LK method (eq 4) and Ambrose method (eq 5). Actual values of critical temperature and pressure as provided in the API Data Book⁴ or DIPPR manual⁵ are available up to C₂₀. For heavier compounds, predicted values of T_c and P_c should be used in eqs 4 and 5, and predicted vapor pressure depends on the method used for estimation of the input parameters. The main objective of our proposed method (eq 11) is for prediction of vapor pressure of very heavy compounds. The operating temperature in a petroleum reservoir or process equipment is well below the critical temperature of such heavy compounds, and the main application of the proposed method will be at temperatures below the critical temperature. For this reason the condition of

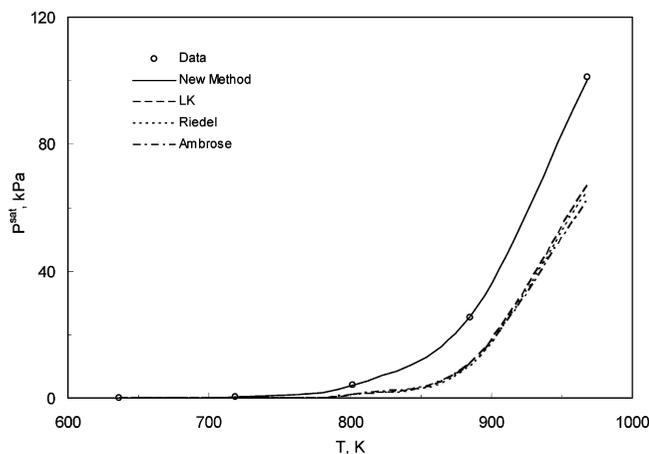
Table 3. Evaluation of Various Methods for Estimation of Vapor Pressure of Different Hydrocarbon Groups in Absolute Error

C_n range	AAD, kPa				MAD, kPa				no. of data points ^{a,c}
	proposed method (eq 11)	Lee–Kesler (eq 4)	Riedel (eq 6)	Ambrose (eq 5)	proposed method (eq 11)	Lee–Kesler (eq 4)	Riedel (eq 6)	Ambrose (eq 5)	
<i>n</i> -Paraffins									
C_1 – C_{50}	3.51	2.01	2.51	2.11	110.86	112.49	112.63	113.70	250
C_{51} – C_{100}	0.21	2.41	3.03	3.15	3.85	13.17	14.73	15.18	210
C_1 – C_{100}	2.67	2.19	2.75	2.59	156.03	112.49	112.63	113.70	460
<i>n</i> -Naphthenes, <i>n</i> -Alkylcyclohexanes									
C_6 – C_{50}	5.11	4.91	5.58	5.16	472.44	259.96	260.12	257.51	225
C_{51} – C_{89}	0.22	8.42	9.02	9.15	1.71	34.54	36.19	39.06	195
C_6 – C_{89}	4.22	6.54	7.17	7.01	526.45	259.96	260.12	257.51	420
<i>n</i> -Aromatics, <i>n</i> -Alkylbenzenes									
C_6 – C_{50}	2.61	4.45	3.44	3.89	123.51	93.27	93.17	93.09	220
C_{51} – C_{90}	0.23	10.52	9.67	9.29	1.54	60.51	58.94	53.92	200
C_6 – C_{90}	3.34	7.34	6.40	6.46	251.75	93.27	93.17	93.09	420
Overall (All Groups) ^b									
C_1 – C_{100}	2.10	5.26	5.36	5.27	472.4	259.96	260.12	257.51	1300

^a Vapor pressure data reference, Dykyj et al.¹³ ^b The carbon numbers which have the maximum absolute deviation. ^c Based on the first two divided ranges of each group. Lee–Kesler, Ambrose, and Riedel methods are given as eqs 4, 5 and 6, respectively. AAD is the average absolute deviation and MAD is the maximum absolute deviation.

**Figure 4.** Evaluation of methods for vapor pressure of *n*-heptane (C_{100}).**Figure 5.** Evaluation of methods for vapor pressure of *n*-nonacosyl-cyclohexane (C_{35}).

$P_r^{\text{vap}} = 1$ at $T_r = 1$ was not imposed in the development of eq 11 in order to have better predictions for heavier compounds. In fact at $T_r = 1$, eq 11 reduces to $\ln P_r^{\text{vap}} = (a_1 + b_1 + c_1) + (a_2 + b_2 + c_2)r + (a_3 + b_3)r^2$. Theoretically, this expression should be zero for all compounds, but, as shown in Table 1,

**Figure 6.** Evaluation of methods for vapor pressure of *n*-trioctacontyl-cyclohexane (C_{89}).

data on vapor pressure were not available for all compounds at $T_r = 1$. Equations 4 and 5 are exact at the critical point, while eq 7 (for petroleum fractions) is not accurate at the critical point. Equation 7 is mainly applicable at temperatures near the normal boiling point of a petroleum fraction. Evaluation of the proposed method (eq 11) at the critical point for *n*-alkanes from C_1 to C_{20} where experimental data on the critical pressure are available is shown in Figure 11. The average deviation between predicted vapor pressure and actual values at the critical point was 0.7%; however, this deviation tends to increase for heavier compounds although data on P_c for such compounds was not available. For *n*-alkane hydrocarbons from C_{21} to C_{50} the proposed method was evaluated with actual data near the critical point and at $T_r = 0.9$ where data was available as indicated in Table 1. Evaluation of the proposed method (eq 11) as well as Lee–Kesler (eq 4), Ambrose (eq 5), and Riedel (eq 6) for hydrocarbons C_{21} – C_{50} at $T_r = 0.9$ is presented in Figure 12. The average deviations (%AAD) for these methods for the prediction of vapor pressure at $T_r = 0.9$ are 0.69% for the proposed method, 1.88% for Lee–Kesler (LK), 3.65% for Ambrose, and 3.06% for the Riedel method. Evaluation of various methods for the prediction of vapor pressure of *n*-alkylbenzenes at $T_r = 0.95$ is shown in Figure 13, and for all hydrocarbon groups up to C_{50}

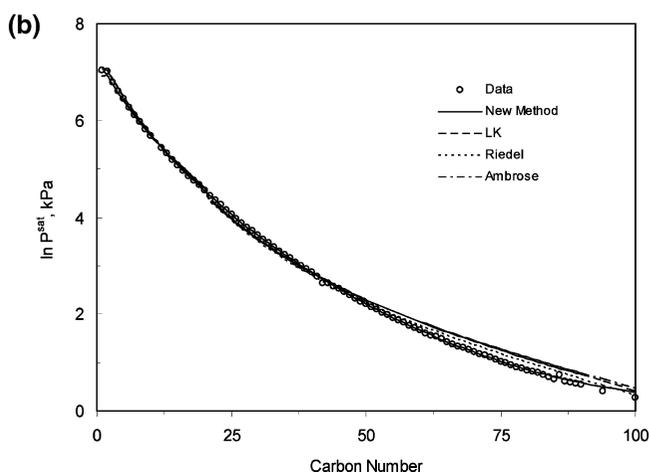
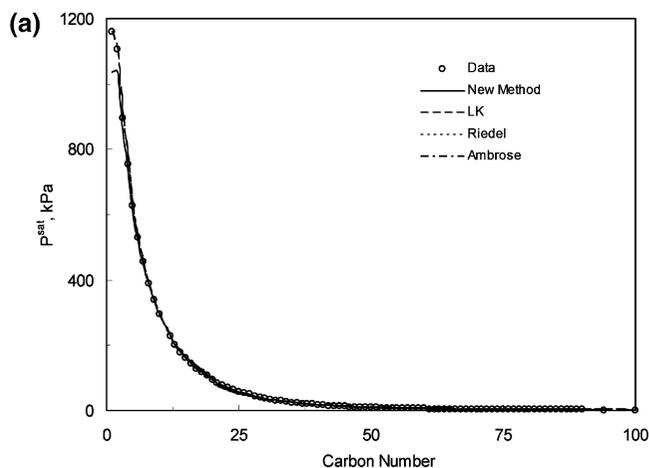


Figure 7. (a) Evaluation of methods for vapor pressure of *n*-alkanes in C_1 – C_{100} range at $T_r = 0.8$; (b) vapor pressure estimation of *n*-alkanes in C_1 – C_{100} range at $T_r = 0.8$ using log scale to show different methods for heavier hydrocarbons.

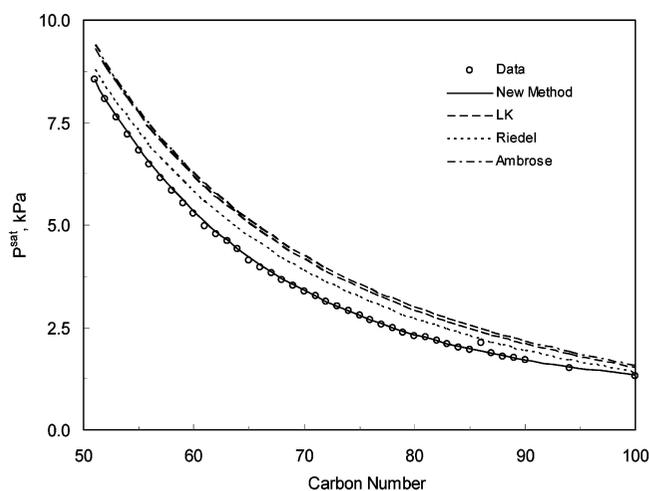


Figure 8. Evaluation of methods for vapor pressure of heavy *n*-alkanes in C_{50} – C_{100} range at $T_r = 0.8$.

a summary of evaluations is presented in Table 4. On the basis of these evaluations, it is fair to say that the proposed method is applicable in the near critical region with good accuracy.

Application to Petroleum Mixtures and Crude Oils

One of the main applications of eq 11 is to predict vapor pressure of petroleum fractions and undefined petroleum

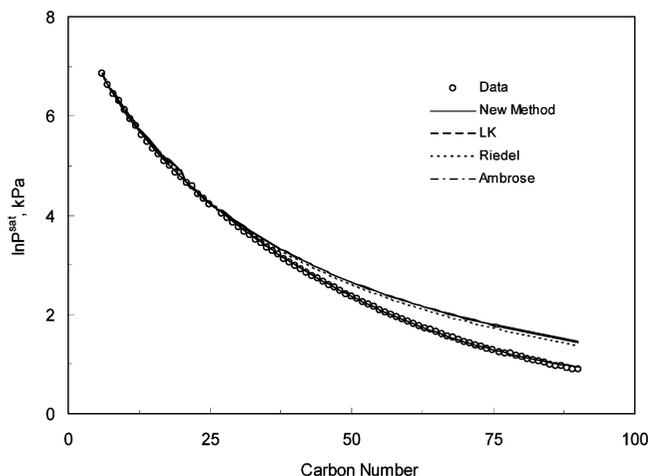


Figure 9. Evaluation of methods for vapor pressure of *n*-alkyl-benzenes in C_6 – C_{90} range at $T_r = 0.8$.

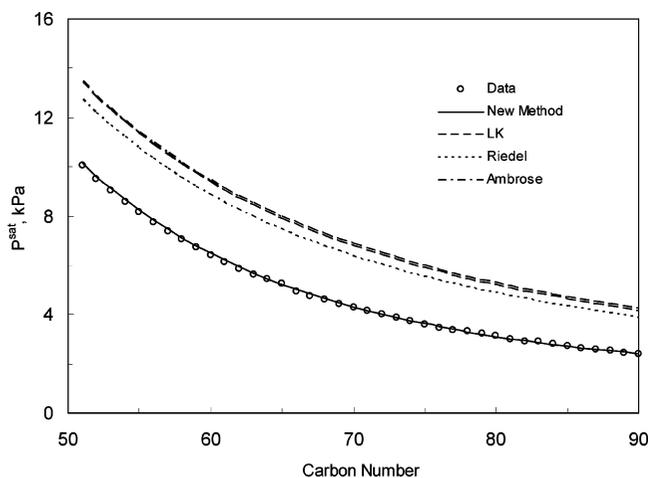


Figure 10. Evaluation of methods for vapor pressure of *n*-alkyl-benzenes in C_{50} – C_{90} range at $T_r = 0.8$.

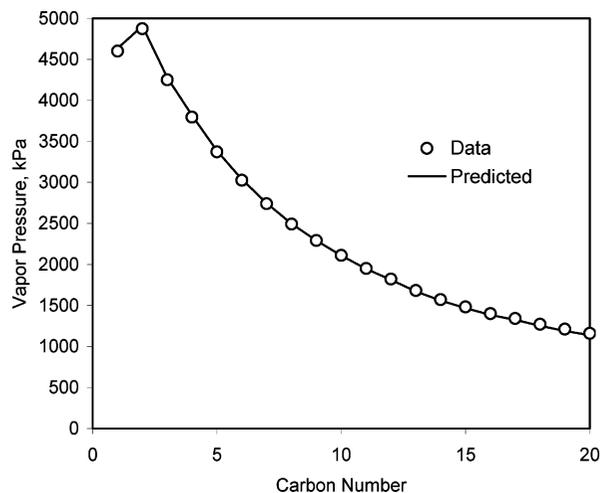


Figure 11. Evaluation of the proposed method (eq 11) for vapor pressure of *n*-alkanes in the C_1 – C_{20} range at the critical point ($T_r = 1$).

mixtures. For a mixture with known composition the following relation is recommended for calculation of vapor pressure.

$$P_{\text{mix}}^{\text{vap}} = x_P P_P^{\text{vap}} + x_N P_N^{\text{vap}} + x_A P_A^{\text{vap}} \quad (12)$$

where, x_P , x_N , and x_A are fractions of paraffins, naphthenes, and aromatics in the mixture and P_P^{vap} , P_N^{vap} , and P_A^{vap} are the

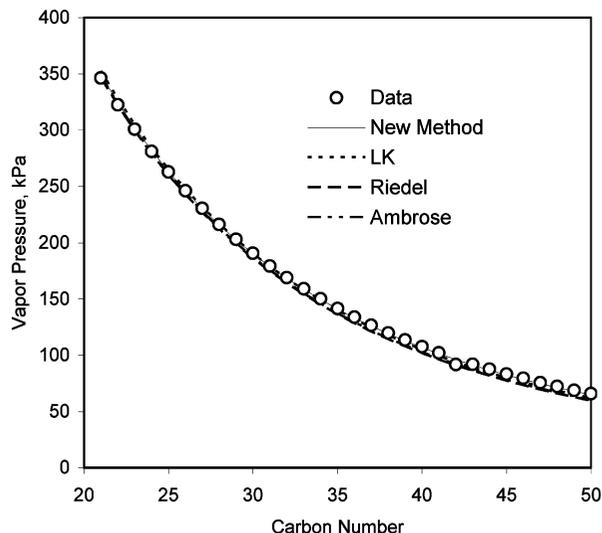


Figure 12. Evaluation of the various methods for prediction of vapor pressure of *n*-alkanes in the C₂₁–C₅₀ range near the critical point ($T_r = 0.9$).

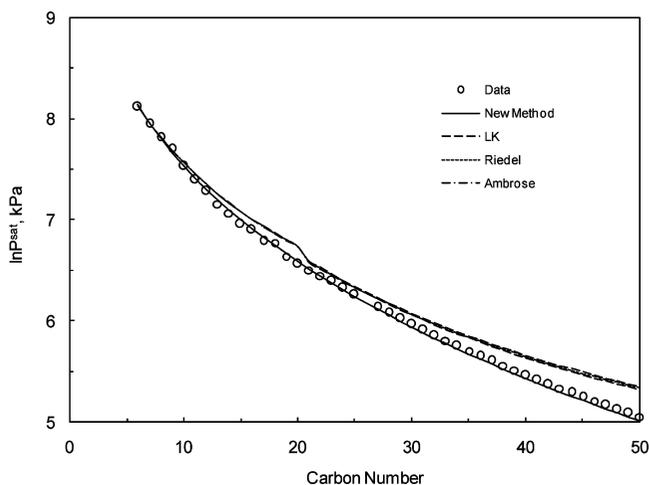


Figure 13. Evaluation of the various methods for prediction of vapor pressure of *n*-alkylbenzenes in the C₆–C₅₀ range near the critical point ($T_r = 0.95$). See Table 4 for other hydrocarbon groups.

Table 4. Evaluation of Various Methods for Estimation of the Vapor Pressure of Different Hydrocarbon Groups at $T_r = 0.95$ (See Figure 13 for Graphical Evaluation of the Methods)

group	C _n range	%AAD			
		new method	LK	Riedel	Ambrose
<i>n</i> -paraffins	C ₁ –C ₅₀	2.09	4.70	4.61	4.54
<i>n</i> -naphthenes, <i>n</i> -alkylcyclohexanes	C ₆ –C ₅₀	4.18	22.56	23.20	23.75
<i>n</i> -aromatics, <i>n</i> -alkylbenzenes	C ₆ –C ₅₀	2.79	15.21	14.16	13.31

corresponding vapor pressures of the three model compounds. The hydrocarbon families that can represent these three groups

Table 5. Evaluation of the New Method for RVP of Petroleum Fractions^a

name	SG	T _b (°C)	data (psi)	new method	AD	Maxwell	AD
gasoline	0.6728	12.8–73.9	12.8	12.39	0.41	12.28	0.52
straight run gasoline	0.6800	36.1–65.0	11.60	9.69	1.91	9.60	2.00
light naphtha	0.6892	20.0–100.0	7.40	6.99	0.41	6.91	0.49
naphtha	0.7217	73.9–104.4	2.50	2.43	0.07	2.39	0.11
heavy naphtha	0.7805	93.3–223.9	0.20	0.14	0.06	0.14	0.06
kerosine	0.8083	160.0–260.1	0.10	0.01	0.09	0.01	0.09

^a Data reference: *Oil and Gas Journal Data Book*; PennWell: Oklahoma, 2000.

Table 6. Evaluation of the Predicted Vapor Pressure of Crude Oils^a

fraction cut	volume %	T _b (°F)	SG	calculated P ^{vap} (psi)
mexican crude, RVP = 6.60 psi				
≤C ₄	1.8			346.32
naphtha	29.0	97–351	0.7146	1.25
kerosine	19.2	351–526	0.8100	4.7 × 10 ⁻³
light gas oil	14.8	526–651	0.8565	1.8 × 10 ⁻⁵
heavy gas oil	24.9	651–1000	0.9123	8.3 × 10 ⁻¹¹
residue	10.3	+1000	1.0078	3.8 × 10 ⁻¹⁶
calculated P _{crude} ^{vap} = 6.60				

^a Data reference: *Oil and Gas Journal Data Book*; PennWell: Oklahoma, 2000.

Table 7. Constants for eq 15 for the Estimation of Input Parameters in eq 11^a

θ	C _n	constants			
		θ _∞	a	b	c
Constants for Physical Properties of <i>n</i> -Alkanes					
T _b (K)	C ₅ –C ₄₀	1070	6.98291	0.02013	2/3
SG	C ₅ –C ₁₉	0.8500	92.22793	89.82301	0.01
d ₂₀ (g/cm ³)	C ₅ –C ₄₀	0.8590	88.01379	85.7446	0.01
I	C ₅ –C ₄₀	0.2833	87.6593	86.62167	0.01
T _{br} = T _b /T _c	C ₅ –C ₂₀	1.1500	-0.41966	0.02436	0.58
-P _c	C ₅ –C ₂₀	0.0000	4.65757	0.13423	0.50
Constants for Physical Properties of <i>n</i> -Alkyl-cyclohexanes					
T _b (K)	C ₆ –C ₂₀	1100	7.00275	0.01977	2/3
SG	C ₆ –C ₂₀	0.845	-1.51518	0.05182	0.7
d ₂₀ (g/cm ³)	C ₆ –C ₂₁	0.840	-1.58489	0.05096	0.7
I	C ₆ –C ₂₀	0.277	-2.45512	0.05636	0.7
T _{br} = T _b /T _c	C ₆ –C ₂₀	1.032	-0.11095	0.13630	0.4
-P _c	C ₆ –C ₂₀	0.000	12.3107	5.53366	0.1
Constants for Physical Properties of <i>n</i> -Alkyl-benzenes					
T _b (K)	C ₆ –C ₄₂	1015	6.91062	0.02247	2/3
-SG	C ₆ –C ₂₀	-0.8562	224.7257	218.518	0.01
-d ₂₀ (g/cm ³)	C ₆ –C ₄₂	-0.8540	238.791	232.315	0.01
I	C ₆ –C ₄₂	-0.2829	137.0918	135.433	0.01
T _{br} = T _b /T _c	C ₆ –C ₂₀	1.0300	-0.29875	0.06814	0.50
-P _c	C ₆ –C ₂₀	0.0000	9.77968	3.07555	0.15

^a References 3, 9. Parameter I is defined as $(n^2 - 1)/(n^2 + 2)$.

are chosen as *n*-alkanes, *n*-alkylcyclohexanes, and *n*-alkylbenzenes. If T_b is the representative boiling point of the mixture (midpoint temperature on the distillation curve), then molecular weights of model components from these groups can be estimated from the following three equations:³

$$M_P = \left(\frac{6.98291 - \ln(1070 - T_b)}{0.02013} \right)^{3/2}$$

$$M_N = \left(\frac{6.95649 - \ln(1028 - T_b)}{0.02239} \right)^{3/2} \quad (13)$$

$$M_A = \left(\frac{6.91062 - \ln(1015 - T_b)}{0.02247} \right)^{3/2}$$

Once M_P, M_N, and M_A from these groups are calculated then the equations provided in Appendix A can be used to estimate the input data needed for eq 11 to calculate P_P^{vap}, P_N^{vap}, and P_A^{vap}, respectively. In cases where the PNA composition is not available, it may be estimated from the method provided in Appendix B using measurable bulk properties.

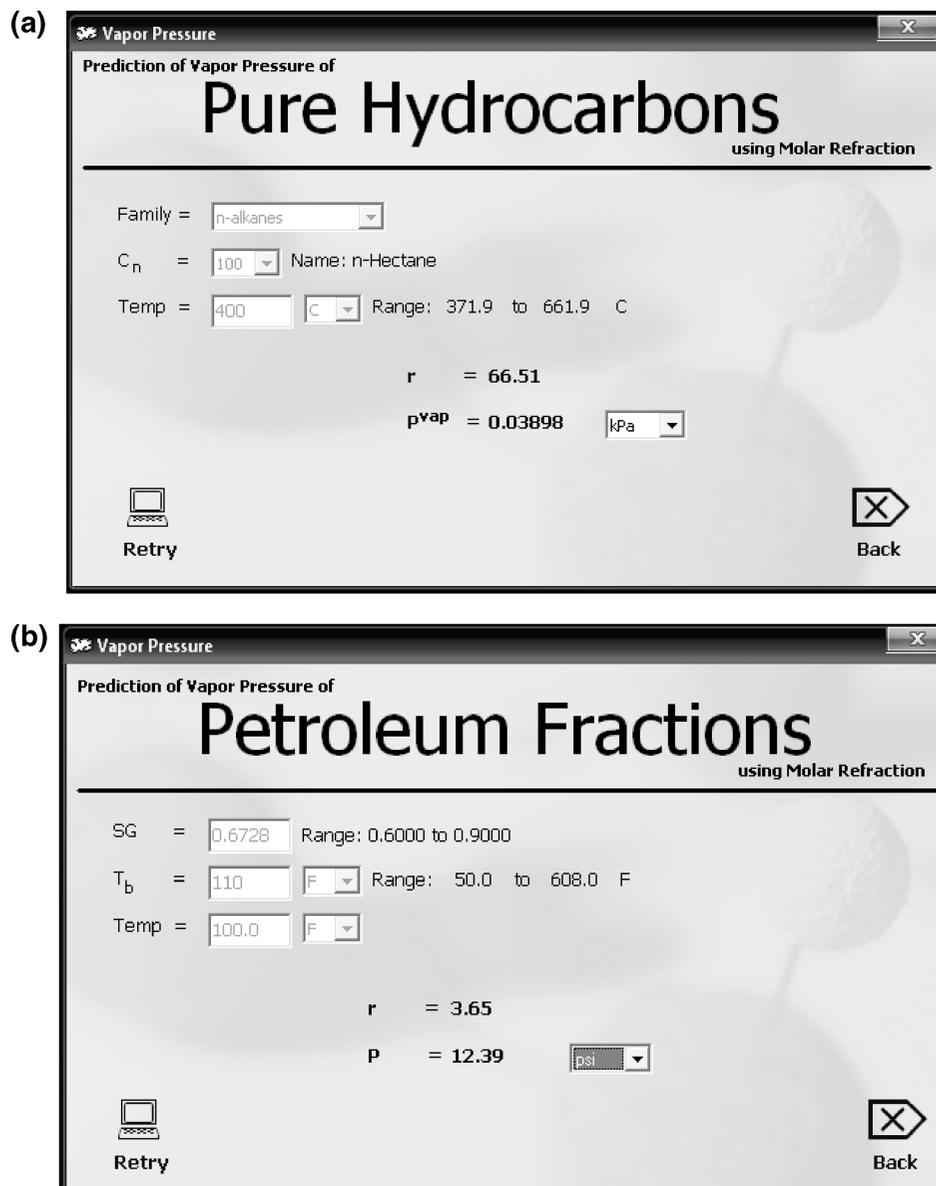


Figure 14. a: A snapshot of the developed PC program for vapor pressure prediction of pure hydrocarbons Figure 14b: A snapshot of the developed PC program for vapor pressure prediction of petroleum mixtures.

As data on true vapor pressure of petroleum mixtures is rarely reported in the literature, the Reid vapor pressure (RVP) which is very close to vapor pressure at 311 K (100 °F) has been used for the evaluation of the proposed method for some petroleum mixtures. Results are shown in Table 5 for six petroleum products and a comparison is made with the Maxwell method (eq 7). The suggested method is slightly superior over the Maxwell method; however, the Maxwell method is specifically developed for light petroleum products and may not be suitable for very heavy residues.

Similarly the method may be applied to more complex and wide boiling range mixtures such as crude oils. For a Mexican crude sample RVP data is given in Table 6 along with composition of fractions generated from the crude. The above method is applied to each fraction, and then the following mixing rule was applied to calculate vapor pressure of the whole crude.

$$P_{\text{crude}}^{\text{vap}} = \sum x_{vi} P_i^{\text{vap}} \quad (14)$$

Results shown in Table 5 indicate that the proposed method may also be used for very wide petroleum mixtures such as crude oils with acceptable accuracy.

Conclusions

The proposed method (eq 11) for calculation of vapor pressure of hydrocarbon systems is applicable to pure hydrocarbons up to *n*-C₁₀₀ with accuracy significantly higher than existing predictive methods. In addition standard methods are suggested for calculation of input parameters when they are not available. The method is also applicable to undefined petroleum fractions (eq 12) as well as crude oils with accuracy comparable with most widely used methods for such mixtures.

Acknowledgment

The authors wish to thank the editors and reviewers for timely review of this manuscript and their useful suggestions.

Appendix

A. Calculation of Input Parameters for the Proposed Method (Equation 11)

The following generalized equation can be used to calculate properties of pure hydrocarbons needed for use in eq 11:

$$\ln(\theta_{\infty} - \theta) = a - bM^c \quad (15)$$

where θ is T_c , P_c , I , or d , and the four constants in the above equation are given in Table 7. These equations can be used for hydrocarbons up to C_{100} as discussed in details in ASTM MNL50.³

B. Calculation of Composition of Petroleum Mixtures

Calculation of vapor pressure through eq 12 requires the knowledge of PNA composition (x_p , x_N , x_A) of a petroleum mixture. For mixtures that such information is not available from laboratory measurements the composition may be estimated using methods available given in the ASTM Manual 50 (Riazi, 2005).

For $M \leq 200$:

$$\begin{aligned} x_p &= 3.7387 - 4.0829SG + 0.014772m \\ x_N &= -1.5027 + 2.10152SG - 0.02388m \\ x_A &= 1 - x_p - x_N \end{aligned} \quad (16)$$

while for $M > 200$:

$$\begin{aligned} x_p &= 1.9842 - 0.27722R_i - 0.15643CH \\ x_N &= 0.5977 - 0.761745R_i + 0.068048CH \end{aligned} \quad (17)$$

where CH is the carbon to hydrogen weight ratio and R_i is the refractivity intercept. Parameters m and R_i are defined as follows:

$$\begin{aligned} m &= M(n - 1.475) \\ R_i &= n - \frac{d}{2} \end{aligned} \quad (18)$$

where n is the refractive index and d is the density (g/cm^3) both at 20 °C. Relations for calculation of M , n , d , and CH are given in Chapter 2 of ASTM Manual 50.³

C. Computer Programs for the Proposed Method

An excel and a Microsoft Windows friendly PC program have been developed for the proposed method. Snapshots of the PC

program for pure hydrocarbons and petroleum fractions are shown in Figure 14 panels a and b, respectively. Readers interested in having a copy of either program may contact the corresponding author to receive a copy.

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Received for review April 12, 2010

Revised manuscript received June 15, 2010

Accepted June 22, 2010

IE100861C