How to Estimate Reid Vapor Pressure (RVP) of Blends

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ABSTRACT

New restrictions on vaporization loss os petroleum products give added emphasis to the measurement of vapor pressure for petroleum fractions and their blends. The common method for measuring vapor pressure is the Reid vapor pressure (Rvp) test. Now an algorithm is available to calculate Rvp without performing the actual test. The algorithm, based on air-and-water free model, uses the Gas Processors Association Soave-Redlich-Kwong equation of state and assumes liquid and gas volumes are additive. Since the calculations are iterative, they are incorporated into a general purpose process simulator to compare predicted values with experimental data. Good agreement is found between predicted and experimental values. Furthermore, the algorithm is fast and can be used to predict Rvp of any hydrocarbon mixture of known composition.

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INTRODUCTION

New restrictions on vaporization loss of petroleum products give added emphasis to the measurement of vapor pressure for petroleum fractions and their blends. The common method for measuring vapor pressure is the Reid vapor pressure (RVP) test. Now an algorithm is available to calculate RVP without performing the actual test.

The algorithm, based on an air- and water-free model, uses the Gas Processors Association Soave-Redlich-Kwong equation of state and assumes liquid and gas volumes are additive. Since the calculations are iterative, they are incorporated into a general-purpose process simulator to compare predicted values with experimental data. Good agreement is found between predicted and experimental values. Furthermore, the algorithm is fast and can be used to predict RVP of any hydrocarbon mixture of known composition.

WHY RVP?

Evaporation losses are related to the true vapor pressure (TVP) of liquids at their storage temperature. Yet the common test for petroleum fractions is the RVP test defined by the American Society for Testing and Materials under the designation ASTM D323-56. The American Petroleum Institute (API) describes the RVP test procedure in detail [1], including the apparatus. Other API publications [2-4] show charts relating RVP and ASTM boiling characteristics of gasolines and crude oils to TVP, a way to estimate RVP of blends, and the relation of RVP to evaporation losses.

THE ALGORITHM

The results from earlier investigators are reviewed in a later section. Their work helped define the relations incorporated in the new algorithm. The iterative procedure calculates the vapor pressure of a liquid fraction for the conditions specified by the RVP test, namely, original sample at 35^{o}F, pressure test started at 60^{o}F, equilibrium vapor/liquid volume of 4 (i.e., $V/L = n = 4$), and final equilibrium pressure measured at 100^{o}F. The algorithm uses the following steps:

Step 1. Calculate the molecular weight of the sample mixture:

$$MW_{mix} = \sum{}_{i} x_i MW_i \qquad (1)$$

Step 2. Evaluate the density of the sample at T = 35, 60, and 100^{o}F. Compute the liquid expansion of the sample using $n = 4$:

$$v_0 = \rho_{60}\left(\frac{n+1}{\rho_{35}} - \frac{1}{\rho_{100}}\right) \qquad (2)$$

Step 3. Make a flash calculation at 100^{o}F. For the first calculation, assume an initial ratio of the equilibrium liquid L and feed liquid F so that $L/F = 0.97$.

Step 4. Using the values from step 3, calculate a new L/F with the equation

$$\frac{L}{F} = \frac{1}{1+\left[\frac{\rho_V MW_L}{\rho_L MW_V}\right]\times\left[v_0 \Big/ \left(1-\rho_V \big/ \rho_{LF}\right)\right]} \qquad (3)$$

Step 5. Use the value of L/F from step 4 to recalculate the flash from step 3 and a new value of L/F from step 4. In most cases, the assumed and calculated values agree within the specified criterion within less than five iterations.

Step 6. The RVP is the flash pressure for the value of L/F obtained by iteration.

The foregoing algorithm is implemented in a simulation package called PROSIM [5], which also includes unit operations, such as distillation, absorption, heat transfer, compression, controllers, recycling, and the capability of defining hypothetical components to represent oil fractions or single pseudocomponents.

APPLICATION EXAMPLES

To demonstrate the accuracy and performance of the algorithm, several examples, taken from the literature, are shown here.

Some of the examples require the characterization of a mixture by pseudocomponents. A hypothetical component, or a pseudocomponent, is usually characterized with a minimum number of properties. In this study, specific gravity, molecular weight, critical temperature, critical pressure, acentric factor, and ideal gas enthalpy are used to define a hypothetical component. The specific gravity is calculated using the smoothed data of Katz and Firoozabadi [6] and Maxwell [7]. The Hariu and Sage correlation [8] is used to represent the molecular weight of petroleum fractions. This correlation can be applied to petroleum fractions with a molecular weight up to 600 and a boiling point up to 1,200^{o}F. Correlations developed by Kesler and Lee [9] are used to calculate the critical temperature and critical pressure of the hypothetical components. These correlations are nearly identical to the results given by the API Data Book [10] to 1,200^{o}F. A correlation presented by Edmister and Lee [11] is used to predict the acentric factor of petroleum fractions. The acentric factor is calculated based on the boiling temperature and the critical temperature. The ideal gas enthalpy is calculated using an integration of the correlation for the ideal gas heat capacity given by Kesler and Lee [9].

Example 1

Precision Scientific [12] supplies a bulletin concerning their Reid vapor pressure automatic apparatus Model RVP-100 showing the RVP value for several samples measured with different apparatus. Their data were obtained from EPA, Michigan.

For a pure component the RVP is equivalent to true vapor pressure at 100^{o}F. Table 1 shows the values reported by Precision Scientific and the values given by the current algorithm for five compounds.

Table 1. Pure component vapor pressure.

	RVP (psi)	
Sample	**Precision Scientific**	**Algorithm**
Cyclohexane	3.37	3.1737
Isooctane	1.86	1.6734
2,2-Dimethylbutane	9.66	9.7392
n-Pentane	15.23	15.4680
3-Methylpentane	6.24	5.9747

Example 2

Bardon and Rao [13] give ASTM distillation curves and RVP values for three gasoline examples, a low and a high volatility and indolene. Table 2 shows the RVP values reported by Bardon and Rao compared with those obtained by the current algorithm. The values for the true vapor pressure and the liquid fraction of the flash at 100^{o}F that satisfy the convergence criterion of the algorithm are also shown. Table 3 shows the ASTM distillation data for the indolene sample given in the article [13]. The results show the method predicts RVP values very accurately, and considering that an equation of state is used to predict the vapor-liquid equilibrium, this procedure can be applied to any sample (with any number of components) of known composition.

Table 2. RVP and TVP for gasoline samples [18].

Gasoline sample	**Measured**	**Bardon and Rao RVP (psi)**	Current Algorithm		
			RVP (psi)	**L/F**	**TVP (psi)**
Low volatility	5.5114	4.3511	6.3849	0.9895	6.6730
Indolene	8.9923	8.7023	8.8763	0.9861	9.3770
High volatility	14.9389	15.6641	13.6240	0.9795	14.4130

Table 3. ASTM data for indolene example [13].

Distilled Vol %	**Temperature (^{o}F)**
Initial point	86.0
10	134.6
20	168.8
30	194.0
40	210.2
50	224.6

60	240.8
70	260.6
80	287.6
90	327.2
End point	388.4

Example 3

Campbell [14] gives the RVP value of a hydrocarbon mixture whose composition is shown in Table 4. He reports an RVP of 18 psi and a TVP of 19.5 psi. Using the current algorithm, the values of the RVP and TVP were found to be 18.252 and 19.995 psi, respectively.

Table 4. Composition of stream for example 3 [14].

Component	**mol%**
i-Butane	9.14
n-Butane	17.10
i-Pentane	9.09
n-Pentane	6.02
n-Hexane	16.84
n-Heptane	41.81
Total	100.00

Example 4

This example is presented to show the influence on the RVP value of a gasoline blend when the amount of butane is incremented in the mixture. Various grades of motor gasoline are specified by ASTM D439-86. The ASTM distillation curve with maximum values of temperatures for the winter season in the Southwest United States is taken from Russell [15]. A set of eight hypothetical components was considered with contents of n-pentane and n-hexane of 25.1694 and 21.7122 mol%, respectively. The value of RVP found was 5.0779 psi, with a liquid fraction of 0.9918 and a TVP value of 5.138 psi. Using computer simulation, it was found that when n-butane is added to the mixture, the RVP increases rapidly. For example, addition of 10 Ib-mol of n-butane to an original 100 Ib-mol mixture gives an RVP value of 8.8714 psi, and addition of 20 Ib-mol increases the RVP to a value of 12.18 psi.

These and other examples show the current algorithm gives RVP values within +/-1.3 psi of those given by other correlations and experimental results.

BACKGROUND FOR THE ALGORITHM

Haskell and Beavon [16] present a method to evaluate the RVP for gasoline blends. The front-end volatility of a blend is calculated with the help of charts that relate the RVP and the 10% evaporated points in ASTM distillation curves. This procedure is limited to the accuracy of the values read from the charts.

Maxwell [7] shows nomograms relating the true vapor pressure with the RVP and the temperature. The slope of the distillation plus loss curve (ASTM) at 10% is used as a parameter to make the nomograms. He also shows a chart relating the TVP with RVP for an extended temperature range from 0 to 180^{o}F.

One of the first theoretical approaches to predict RVP of fuel blends is given by Stewart [17]. His model neglects the presence of air and water vapor in the test. He assumes the volatile components have the molal density of butanes and the nonvolatile components have the thermal expansion characteristics of n-octane. He represents the equilibrium liquid composition in the Reid test as the following equilibrium flash equation:

$$x_i = \frac{F_i}{L + \left[\frac{(\kappa\pi)_i \gamma_i V_V}{Z_V RT}\right]} \qquad (4)$$

His method assumes an evacuated container and takes the absolute pressure as the RVP value, since the system is free of both air and water. Stewart's model is taken as a basis for the algorithm presented here.

Bardon and Rao [13] present an equation to predict vapor pressure and RVP of gasolines using the temperature of the blend and the extent of vaporization as parameters. They assume a behavior that follows the Clausius-Clapeyron equation.

$$P_f = f_1 e^{(-f_2 / T)} \qquad (5)$$

The problem here consists of finding the two functions f_1 and f_2 for the extent of evaporation fraction (*V/F*) of a particular gasoline sample.

Bardon et al. [18] present a method or experimental program to evaluate the vapor pressure of a gasoline over a range of temperatures and extent of evaporation. They show the validity of their model by comparing predicted and measured vapor pressure values for three samples of gasoline: low volatility, indolene, and high volatility.

Soave [19] represents the pressure-volume-temperature behavior of pure substances as

$$P = \frac{RT}{v-b}\left[\frac{aT}{v}(v+b)\right] \qquad (6)$$

where:

$$a_i T = a_{ci} \alpha_i \qquad (7)$$

$$a_{ci} = \frac{0.4274 R^2 T_{ci}^2}{P_{ci}} \qquad (8)$$

$$b_i = \frac{0.08664 R T_{ci}}{P_{ci}} \qquad (9)$$

To reproduce the vapor pressure of nonpolar and slightly polar substances, Mathias [20] expresses α_i as

$$\alpha_i^{0.5} = 1 + m_i\left(1 - T_{Ri}^{0.5}\right) - p_i\left(1 - T_{Ri}\right)\left(0.7 - T_{Ri}\right) \qquad (10)$$

where the reduced temperature T_{Ri} of a component *i* is equal to T/T_{ci}. Also *m* is a function of the acentric factor ω, defined as

(11)

$$m_i = 0.48508 + 1.55171\omega_i - 0.15613\omega_i^2$$

At supercritical temperatures, the following relation was suggested by Boston and Mathias [21]:

$$\alpha_i^{0.5} = e^{c_i\left(1 - T_{Ri}^{d_i}\right)} \tag{12}$$

where:

$$d_i = 1 + \frac{m_i}{2} + 0.3p_i \tag{13}$$

$$c_i = \frac{d_i - 1}{d_i} \tag{14}$$

For mixtures, the parameters *a* and *b* are determined by a combining rule proposed by the Gas Processors Association [22], as follows:

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{15}$$

$$b = \sum_i x_i b_i \tag{16}$$

and

$$a_{ij} = [a_i a_i]^{0.5}[l - k_{0,aij} - k_{1,aij}(T / 1{,}000)] \tag{17}$$

where k_0 and k_1 are the binary interaction parameters used to represent the vapor-liquid equilibria of binary mixtures. Values of the interaction parameters are taken from *Dechema Chemistry Data Series* [23] when they are available. Otherwise, experimental data from the GPA VLE Data Bank [24] are fitted to the equation of state.

The new algorithm can be seen as a flash process. The material balance is represented by the equation

$$F = V + L \tag{18}$$

where *F* is the feed to the flash and the products are a vapor *V* and a liquid *L*.

If ρ is the density and *v* is the volume of a blend of molecular weight *MW*, the subscripts *L* and *V* are used to reference the liquid and gas phases to rewrite Eq. (18) as follows:

$$F = \frac{\rho_L v_L}{MW_L} + \frac{\rho_V v_V}{MW_V} \tag{19}$$

As in the case depicted by Stewart [17], the sample is assumed to be free of air and water vapor during the Reid test. Consequently, the sample is supposed to be initiated with an evacuated bomb and the RVP is given by the pressure at equilibrium. To have a measure of the liquid expansion of the sample and to correct the phase volumes for thermal expansion and evaporation, the following assumptions are made.

Before the RVP test, the mixture is at a constant temperature of 35°F. At the beginning of the test, the temperature is 60°F. Then, during the test, the temperature is held constant at 100°F. At this point, evaporation is neglected.

Taking 1 ft^3 at 60°F as a basis for the calculation and considering the ratio *V/L* = *n*, the volume of the gas phase corrected for the liquid expansion is given by

$$v_0 = \left[n \frac{(M/\rho)_{35}}{(M/\rho)_{60}} \right] - \frac{(M/\rho)_{100} - (M/\rho)_{35}}{(M/\rho)_{60}} \tag{20}$$

where *M* is the mass of the sample that has been evaporated and *n* = *V/L* (4 in this case). Equation (20) can be rewritten as

$$v_0 = \{n\, \rho_{60} / \rho_{35}\} - \rho_{60}\{[1/\rho_{100}] - [1/\rho_{100}]\} \tag{21}$$

which is simplified to give the algorithm equation

$$v_0 = \rho_{60} \left(\frac{n+1}{\rho_{35}} - \frac{1}{\rho_{100}} \right) \tag{2}$$

The gas-phase volume after the liquid expansion, assuming the phase volumes to be additive, is given by

$$v_V = v_0 + v_V \frac{\rho_V}{\rho_L} \tag{22}$$

or

$$v_V = \frac{v_0}{1 - \rho_V / \rho_L} \tag{23}$$

Substituting Eq. (23) into Eq. (19) and rearranging, the liquid fraction of the flash is given by the algorithm equation

$$\frac{L}{F} = \frac{1}{1 + \left[\frac{\rho_v MW_L}{\rho_L MW_v} \right] \times \left[v_0 \Big/ \left(1 - \rho_v \big/ \rho_{LF} \right) \right]} \tag{3}$$

where ρ_{LF} is the density of the liquid feed at 100°F. This liquid fraction is used by the algorithm to obtain the RVP of a mixture.

NOMENCLATURE

a,b,c,d,p	constants for equation of state
F	feed to flash
f_1,f_2	functions of extent of evaporation
k	interaction parameter for equation of state
L	liquid from flash
M	total mass
MW	molecular weight
m	function of acentric factor
n	value of ratio V/L
P	pressure
p	polar parameter
R	universal gas constant
RVP	Reid vapor pressure
T	temperature
V	vapor from flash
v	volume
x	equilibrium liquid composition
Z	gas compressibility factor

Greek Letters

ω	temperature dependent parameter for equation of state
γ	activity coefficient
$\kappa\pi$	ideal vapor/liquid equilibrium activity coefficient
ρ	density
Σ	summation
ω	acentric factor

Subscripts

C	critical property
i	component *i*
ij	mixture *ij*
j	component *j*

L	liquid phase
R	reduced property
V	vapor phase

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