

CORRELATION EQUATIONS TO PREDICT REID VAPOR PRESSURE AND PROPERTIES OF GASEOUS EMISSIONS FOR EXPLORATION AND PRODUCTION FACILITIES

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
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Correlation Equations to Predict Reid Vapor Pressure and Properties of Gaseous Emissions for Exploration and Production Facilities

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4683

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ABSTRACT

Operators of petroleum storage tanks often need to prepare site-specific emission inventories to meet environmental regulations. Emission inventories can be quite complicated to prepare, and often necessitate laboratory analyses of oil and gas samples in order to quantify key variables such as Reid Vapor Pressure (RVP), gas molecular weights, hazardous air pollutant species (HAPs) distributions, and specific gravity of the separator gas. This report establishes simple techniques to estimate these variables in the absence of laboratory data. Analyses were performed of emissions measurements, oil and gas sampling results, and emissions modeling results for more than 100 crude oil exploration and production (E&P) storage tanks. In conclusion, correlation equations or statistical averages are recommended in order to estimate RVP, vented flash gas molecular weight, vented working and standing gas molecular weight, hydrocarbon speciation (including HAPs), and separator gas specific gravity.

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EXECUTIVE SUMMARY

It is necessary to estimate certain physico-chemical properties of oil and emitted gases in order to construct an emission inventory for a crude oil storage tank. These properties include (1) the Reid Vapor Pressure (RVP) of sales oil, (2) the molecular weights of gases emitted from flash processes and storage tanks, (3) the mole fractional contributions of hydrocarbons and hazardous air pollutants (HAPs) to gaseous emissions, and (4) the specific gravity of the separator gas. Laboratory analyses of oil and gas samples are necessary in order to determine the RVP and gas properties accurately. However, laboratory analyses are often costly or difficult to obtain. This report establishes simple techniques, such as correlation equations or statistical averages, to estimate these variables in the absence of laboratory data.

In this analysis, physico-chemical data and operational parameters for 103 crude oil exploration and production (E&P) storage tanks were examined. (American Petroleum Institute [API] provided data for the 103 tanks.) Linear regression analyses were performed in order to explore correlations of RVP and gas properties with easily measured or judged parameters, such as separator pressure (SP), separator temperature (ST), sales oil API gravity (APIG), and the fractional contribution of non-hydrocarbons to total emissions (%nonHC_{TOT}) (e.g., percent CO₂ plus H₂S by volume). Emission estimates based on these simple correlations were compared to estimates that were calculated with (1) the E&P TANK software package, (2) laboratory analyses of oil and gas samples, and (3) analyses of vent gases and directly measured flow rates. In conclusion, several correlation equations and statistical averages were recommended for use as explained below.

Reid Vapor Pressure (RVP).

If only the API gravity (APIG) of the sales oil is known:

$$\text{RVP} = -1.699 + 0.179 \text{ APIG}$$

(Equation ES-1)

If the APIG and the bubble point (BP) of the sales oil are both known:

$$\text{RVP} = -2.596 + 0.417 \text{ BP} + 0.119 \text{ APIG}$$

(Equation ES-2)

ES-1

Molecular Weight of W&S Gas. An average value of 50 lb/lb-mole that was established by earlier research is recommended for continued use.

Molecular Weight of Flash Gas (MW_F).

$$\text{MW}_F = -0.351 - 0.013 \text{ SP} + 0.193 \text{ ST} + 0.453 \text{ APIG} + 0.360 \% \text{nonHC}_{\text{TOT}}$$

(Equation ES-3)

Mole Fractional Contributions of Hydrocarbons and HAPs. Since many of the correlations developed for HAP speciation were weak or uncertain, the average speciation profiles are recommended for use (see Table ES-1).

Table ES-1. Average speciation profiles, mole percent.

Species	Flash Gas – Mean Mole Percent Contribution	W&S Gas – Mean Mole Percent Contribution
	Percent of THC	Percent of THC
CH ₄	41.00	22.36
C ₂ H ₆	16.87	20.49
C ₃ H ₈	18.35	28.00
i-C ₄ H ₁₀	5.21	6.83
n-C ₄ H ₁₀	8.67	10.92
i-C ₅ H ₁₂	3.27	3.72
n-C ₅ H ₁₂	2.77	3.17
Hexanes	1.15	1.30
Heptanes	1.07	1.26
Octanes	0.45	0.54
Nonanes	0.10	0.13
Benzene	0.14	0.18
Toluene	0.11	0.15
Ethylbenzene	0.00	0.01
Xylenes	0.03	0.04
n-Hexane	0.78	0.90
Pentanes+	0.00	0.00

Specific Gravity of the Separator Gas. The following equation is recommended to predict the specific gravity of the separator gas when laboratory results are unavailable.

$$\ln(SG_{SG}) = -0.476 - 0.102 \ln(SP) + 0.003 ST + 0.008 APIG + 0.011 \%nonHC_{TOT}$$

(Equation ES-4)

Section 1

INTRODUCTION

Exploration and production (E&P) storage tanks are industrial sites constructed for the extraction and temporary storage of petroleum. Figure 1-1 illustrates operations and equipment at a typical E&P storage tank. Freshly extracted crude oil first enters a separator that removes water from the oil stream. Within the separator (1), volatile organic gases escape from the crude oil. Normally, a combustion device disposes of the separator gas. A pressure drop occurs across the flash valve (2) resulting in flash emissions. At some storage tanks, a blanket gas (3) joins the crude oil stream as it enters the storage tank. A temporary storage tank (4) contains the crude oil until sale and transfer.

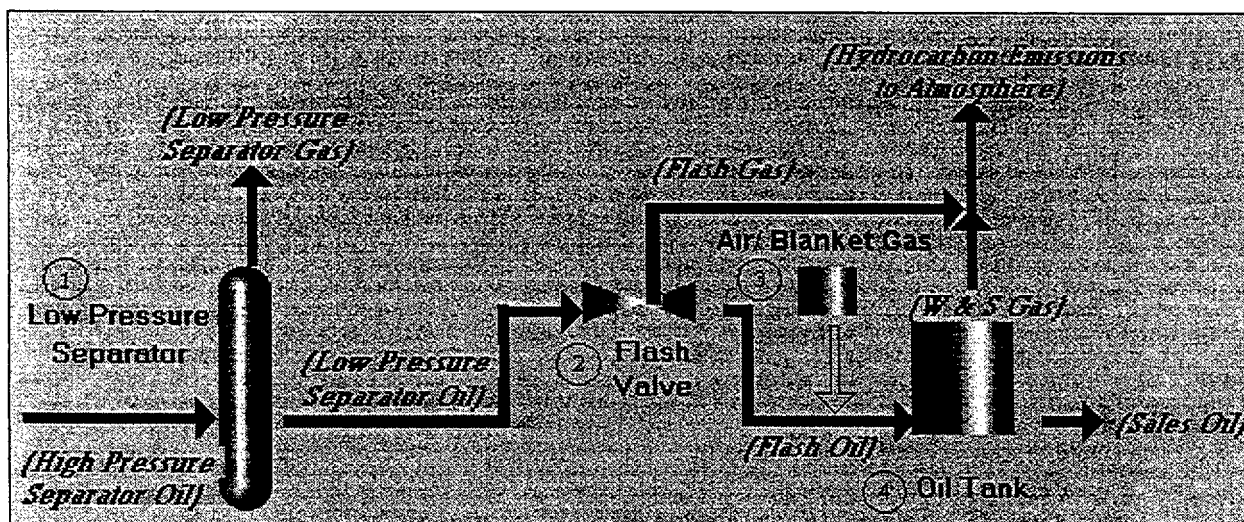


Figure 1-1. Illustration of crude oil extraction and storage processes at an exploration and production storage tank (American Petroleum Institute, 1997a).

The hydrocarbon emission inventory for an E&P storage tank includes working and standing (W&S) losses and flashing losses. W&S emissions arise from changes in the storage tank liquid level, in the atmospheric temperature, or in the barometric pressure that force gases out of the tank vapor space. Flash emissions result when a large pressure drop occurs and dissolved gases escape from the liquid oil stream, similar to the way that carbon dioxide escapes from an opened can of soda pop.

It is necessary to estimate certain physico-chemical properties of oil and emitted gases in order to construct an emission inventory for an E&P storage tank. These properties include (1) the Reid Vapor Pressure (RVP) of sales oil, (2) the molecular weights of gases emitted from flash processes and storage tanks, (3) the mole fractional contributions of hazardous air pollutants (HAPs) to gaseous emissions, and (4) the specific gravity of the separator gas. Laboratory analyses of oil and gas samples are necessary in order to determine the RVP and gas properties accurately. However, when laboratory results are unavailable, the use of default values allows rough estimation of emissions. These default values are constant, although the variables they represent are known to differ among storage tanks. The purpose of this analysis is to replace the default values with simple correlations that only require easily measured inputs. These correlations are intended to increase the accuracy of emission inventories for E&P storage tanks.

OVERVIEW OF THE VARIABLES AND THEORETICAL CONTEXT

The Reid Vapor Pressure (RVP) is a measure of the volatility of a petroleum product. Sales oil RVP is a key parameter needed to estimate W&S emissions from crude oil storage tanks because it is related to the quantity of hydrocarbon vapors present in the vapor headspace of the storage tank. When laboratory tests are unavailable, current practice calls for the use of a default value ($RVP = 5$ psia) in order to estimate W&S losses from crude oil storage tanks. Section 3 presents an analysis of RVP and an equation that may be used instead of the default value to predict RVP.

The average molecular weights of the hydrocarbon fractions of the W&S gas (MWT_{ws}) and of the flash gases (MWT_F) must be estimated in order to calculate W&S losses and flashing losses. In both cases, default values of 50 lb/lb-mol are currently used in the absence of laboratory analyses. The default value for MWT_{ws} was established by the American Petroleum Institute (API) through a significant research effort (American Petroleum Institute, 1991). The analysis described in this report addresses MWT_{ws} (Section 4) in order to compare results with API's previous research. A favorable comparison (1) confirms that the group of storage tanks analyzed in the report is similar and representative of API's previous research, and (2) enhances API's past research (American Petroleum Institute, 1991).

Due to a lack of available information, the current default value for MWT_F was selected somewhat arbitrarily. Given a basic understanding of E&P operations, it was recognized that the flash gases should consist of lighter compounds than the W&S gases. Therefore, the default value for MWT_{WS} (50 lb/lb-mol) was expected to represent an upper limit to MWT_F . The use of this default value for MWT_F tends to produce conservatively high estimates of flash emissions. Section 4 of this report presents an analysis of MWT_F and a correlation equation intended to replace the default value.

In order to estimate emissions of hazardous air pollutants from an E&P storage tank, it is necessary to estimate their contributions to the inventory as fractions of total hydrocarbon (THC) emissions. The U.S. EPA has established speciation profiles derived from source tests at E&P storage tanks (U.S. Environmental Protection Agency, 1990). The goal of this analysis is to provide an alternative means to estimate HAP mole fractions for emissions at E&P storage tanks (Section 5). The HAPs that are included in this discussion are benzene, ethylbenzene, hexane, toluene, and xylenes.

The RVP of sales oil and the compositions of gaseous emissions from an E&P storage tank depend upon the composition of the fresh crude extract and the storage tank's operational parameters. These relationships are highly complex. Freshly extracted crude petroleum is a multicomponent mixture containing inorganic compounds (H_2S and CO_2) and organic compounds (methane, ethane, and many hydrocarbons). Below, Treybal (1980) comments on the complexities involved with predicting the behaviors of multicomponent mixtures.

Many of the multicomponent systems of industrial importance can be considered nearly ideal... This is particularly true for hydrocarbon mixtures of the same homologous series... In such cases, Raoult's law, or its equivalent in terms of fugacities, can be applied and the gas phase equilibria calculated from the properties of the pure components. But it is generally unsafe to predict detailed behavior of a multicomponent system from consideration of the pure components alone, or even from a knowledge of the simple binary systems that may be formed from the components.

In essence, Treybal's remarks indicate that it is difficult to successfully apply simple physical theories in order to predict the behavior of a multicomponent mixture (such as petroleum), even when the exact chemical composition of the mixture is known. An empirical approach is an alternative to theoretical predictions. For example, this analysis statistically investigates simple correlations among RVP, gaseous emissions, and parameters that are easily measurable at E&P storage tanks. Predictions that are based on such correlations are empirical in nature, rather than theoretical. A few assumptions are necessary in order to apply this empirical analysis, which covers a small data set, to a wider population. These assumptions include (1) that most fresh crude extracts are relatively similar in composition, and (2) that differences in their volatilities can be predicted by a few easily measured parameters (e.g., the API Gravity of the sales oil, the operating temperature and pressure of the separator, or others).

APPROACH

In this analysis, physico-chemical data and operational parameters for 103 E&P storage tanks were examined (Section 2). (Data for the 103 tanks were provided by the API.) Linear regression analyses were performed in order to explore correlations of RVP and gas properties (Sections 3 through 6) with other storage tank parameters. Emission estimates based on these simple correlations were compared to estimates that were calculated with (1) the E&P TANK software package, and (2) laboratory analyses of oil and gas samples (Section 7). In conclusion, correlation equations were recommended for use in the future (Section 8).

Section 2

REVIEW OF THE DATA

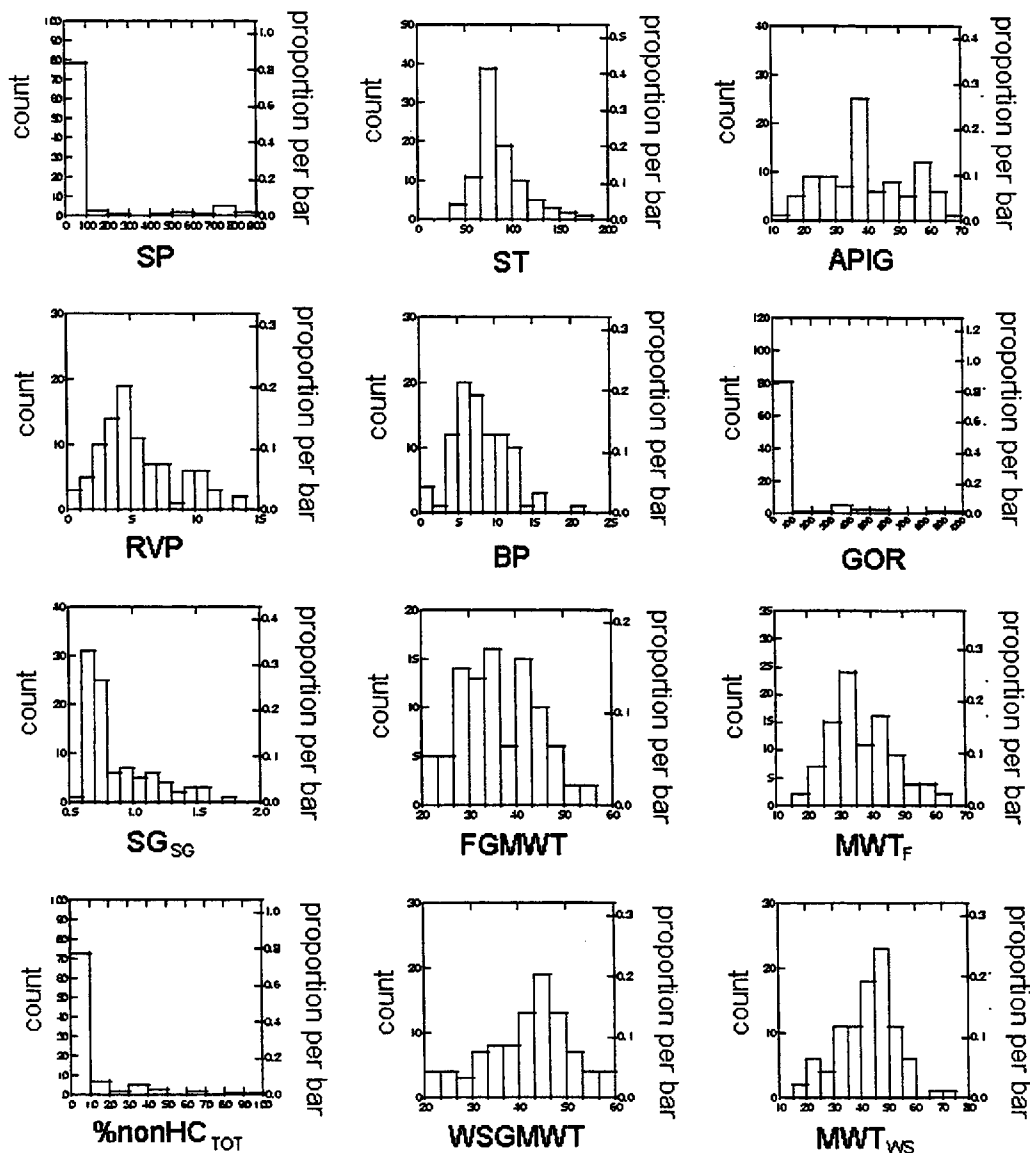
Initially, E&P TANK was used to model emissions and some physico-chemical parameters for all 103 E&P storage tanks. Upon review of the model output, the results were found to be unusual for 16 of the tanks (Table 2-1). Eight of these were excluded from the analysis because E&P TANK could not resolve some of the output parameters intended for use in this analysis (such as the flash gas or the W&S gas molecular weights). One appeared to be duplicated in the data set; only one of the repeated cases was retained. Ninety-four storage tanks remained in the data set for analysis.

Table 2-1. Results of an initial examination of E&P TANK model output for 103 E&P storage tanks.

Reason that results were unusual	Problem Resolution	Defining Tank Parameters			
		Separator Pressure (psig)	Separator Temperature (°F)	Sales Oil APIG (°API)	Sales Oil RVP (psia)
Model diverged.	Excluded.	8	154	23	0.2
Separator oil specific gravity was unrealistically low.	Re-ran E&P TANK with AP-42 option and replaced the unusual specific gravity data.	42	110	39	5.4
		66	83	40	3
		60	60	44	10.1
		41	72	45	5.2
		40	76	47	10.6
		870	78	57	13.1
		110	72	59	10
No flash emissions.	Excluded.	17	106	20	3.3
No W&S emissions.	Excluded.	15	120	19	4.8
		280	106	30	4.8
		40	110	34	3.2
		95	118	42	8.1
		50	125	49	8.9
		170	75	68	12.5
Duplicate case.	Excluded repeated data.	60	58	39	6.8

Figure 2-1 illustrates the general properties of the data set encompassing the remaining 94 storage tanks. It is apparent that the data for the separator pressure (SP), specific gravity of the separator gas (SG_{SG}), gas-to-oil ratio (GOR), and mole fraction of non-hydrocarbons in the vent gas ($\%nonHC_{TOT}$) are skewed and are probably best modeled with lognormal distributions. The rest of the parameters generally appear to follow a normal distribution, or “bell curve”.

Figure 2-2 is a scatter plot matrix of the same parameters illustrated in Figure 2-1. A scatter plot matrix is a visual tool that helps identify correlations among large numbers of variables. In Figure 2-2, several correlations are apparent (for example, sales oil RVP vs. APIG; $\ln(GOR)$ vs. sales oil APIG).



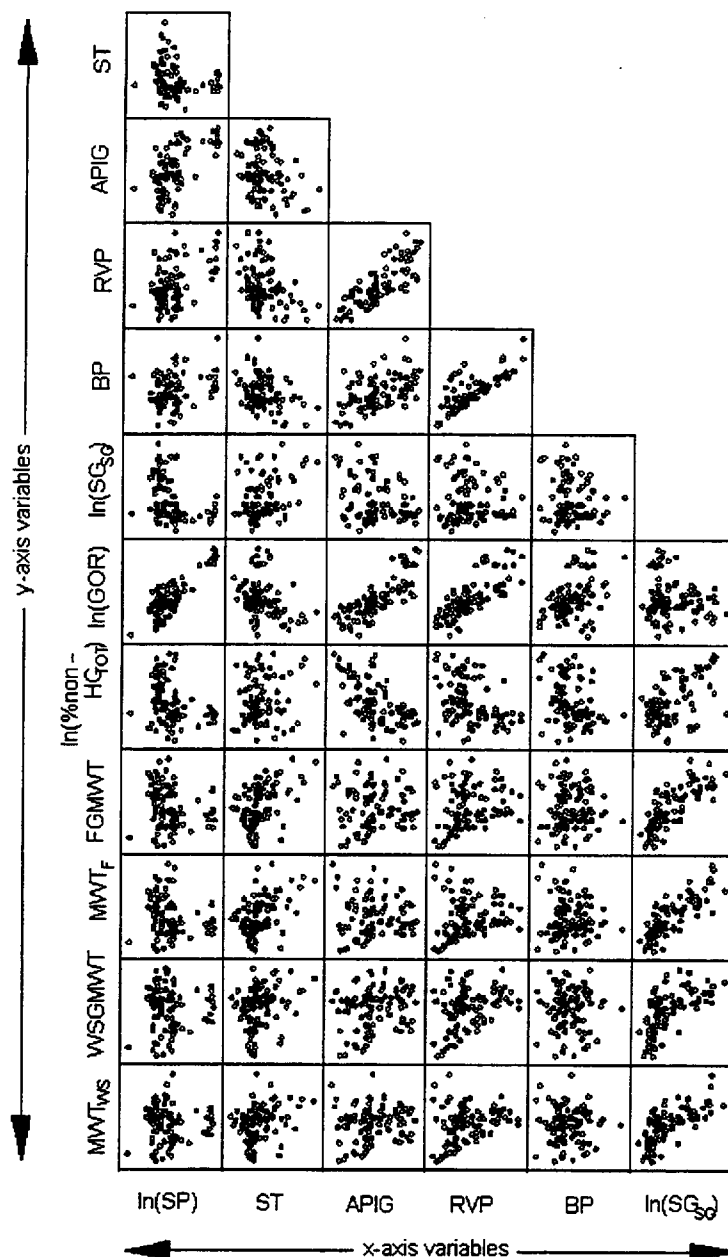
Measured Parameters

SP = Separator pressure (psig)
 ST = Separator temperature ($^{\circ}$ Rankine)
 APIG = Sales oil APIG ($^{\circ}$ API)
 RVP = Sales oil RVP (psia)
 BP = Sales oil bubble point (psia)
 SG_{SG} = Specific gravity of the separator gas

Modeled Parameters

GOR = Gas-to-oil ratio of the sales oil (scf/bbl)
 FGMWT = Flash gas total molecular weight (lb/lb-mol)
 MWT_F = Molecular weight of the THC fraction of the flash gas (lb/lb-mol)
 %nonHC_{TOT} = Sum mole fraction of the non-hydrocarbon species in the total vent gas (%); total vent gas = W&S gas + flash gas
 WSGMWT = W&S gas total molecular weight (lb/lb-mol)
 MWT_{WS} = Molecular weight of the THC fraction of the W&S gas (lb/lb-mol)

Figure 2-1. Frequency distributions of selected parameters for the 94-tank data set.



Measured Parameters

SP = Separator pressure (psig)
 ST = Separator temperature ($^{\circ}$ Rankine)
 APIG = Sales oil APIG ($^{\circ}$ API)
 RVP = Sales oil RVP (psia)
 BP = Sales oil bubble point (psia)
 SG_{S_0} = Specific gravity of the separator gas

Modeled Parameters

GOR = Gas-to-oil ratio of the sales oil (scf/bbl)
 FGMWT = Flash gas total molecular weight (lb/lb-mol)
 MWT_F = Molecular weight of the THC fraction of the flash gas (lb/lb-mol)
 $\%nonHC_{TOT}$ = Sum mole fraction of the non-hydrocarbon species in the total vent gas (%); total vent gas = W&S gas + flash gas
 WSGMWT = W&S gas total molecular weight (lb/lb-mol)
 MWT_{WS} = Molecular weight of the THC fraction of the W&S gas (lb/lb-mol)

Figure 2-2. Scatter plot matrix of selected parameters for the 94-tank data set. Each cell of the matrix is a scatter plot (x vs. y). y-Axis variables are on the left side of the matrix; x-axis variables are below. A scatter plot matrix is a visual aid to identify correlations; units of measure are unnecessary for this purpose.

Section 3

ANALYSIS OF REID VAPOR PRESSURE

The purpose of this section is to establish a correlation equation that predicts the sales oil RVP. Several measured parameters are discussed, including sales oil RVP, sales oil APIG, sales oil bubble point, separator temperature, and separator pressure.

UNDERLYING THEORY

RVP is a composite value of the vapor pressures exerted by individual components in a gas phase that is in equilibrium with a liquid mixture. For a simpler scenario, that of a pure liquid, the Antoine equation correlates pure substance vapor pressure (p^*) with temperature (Felder and Rousseau, 1978).

$$\log_{10} p^* = A - B/(T + C) \quad (\text{Equation 3-1})$$

A, B, and C are constants determined from a least squares fit of measured data. The RVP of a mixture may be estimated by combining the contributions of individual species to the total vapor pressure. This requires an assumption that species' individual contributions may be predicted from their behaviors as pure substances. This assumption often introduces a large degree of error.

$$\text{RVP} = \sum y_i 10^{[A - B/(T + C)]} \quad (\text{Equation 3-2})$$

where y_i is the mole fraction of component i in the gas phase. A, B, and C are constants that are species dependent. Protocol calls for measurements of RVP to be reported at a constant temperature of 560° Rankine (°R); therefore, Equation 3-2 may be simplified as

$$\text{RVP} = \sum y_i a_i \quad (\text{Equation 3-3})$$

where a_i is a species-specific constant defined by $10^{[A - B/(560^\circ\text{R} + C)]}$. Equation 3-3 indicates that RVP is related to the mole fractions and species-specific constants of each gas phase component. Although Treybal (1980) cautions against models that treat mixtures as though they were analogous to pure substances, this equation (3-3) represents the best simplified theory currently available.

EXPECTED EMPIRICAL RELATIONSHIPS

Predictors of sales oil RVP are expected to directly relate to the volatility of the sales oil or the conditions of the storage tank (such as sales oil APIG and bubble point). (Measurements of separator pressure and temperature are collected in a vessel external to the sales oil tank, and therefore, are not expected to correlate well with the RVP of the sales oil.)

The bubble point pressure is defined as the pressure at which the first bubble of vapor will form in a liquid that is held in a closed container at a constant temperature. The bubble point pressure of the sales oil is very likely to correlate well with the RVP since (1) both variables represent a pressure measurement of the gas phase in equilibrium with the sales oil, and (2) the bubble point pressure represents the theoretical upper limit to RVP. Figure 3-1 illustrates the relationship between sales oil bubble point and RVP for 94 E&P storage tanks. The fact that none of the data points exceeds the 1:1 line (which would represent perfect agreement) illustrates that the bubble point is the upper limit for the RVP. The bubble point, however, was not considered to be a parameter that could be measured easily at an E&P storage tank. Therefore, it is recommended for use only as an optional input variable.

DESCRIPTIVE STATISTICS

Table 3-1 summarizes key descriptive statistics for the sales oil RVP, separator pressure and temperature, and sales oil APIG associated with the 94 E&P storage tanks considered in this analysis. (Note that the RVP and APIG data were measured at a fixed temperature of 100°F, even though the tank temperatures or ambient temperatures probably varied significantly.)

Currently, API employs a default value ($RVP = 5$ psia) in order to estimate working and standing (W&S) losses from crude oil storage tanks. The goal of this analysis is to improve upon the default assumption.

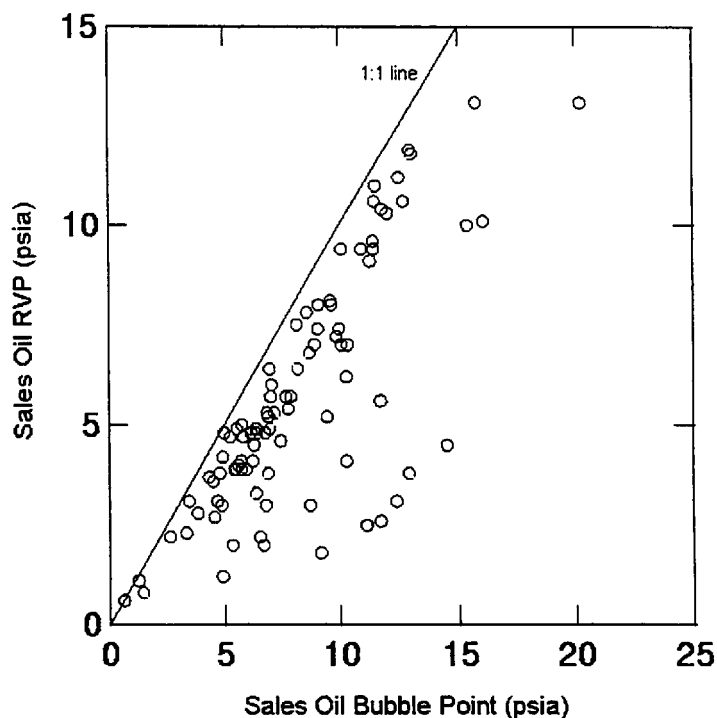


Figure 3-1. The relationship between RVP and bubble point observed at 94 E&P storage tanks. The bubble point is the upper limit to RVP.

Table 3-1. Descriptive statistics of variables used to predict RVP.

Statistic	RVP (psia @ 100°F)	SP* (psig)	ln(SP)**	ST (°F)	APIG (°API @ 100°F)
Minimum	0.60	4.0	1.39	40	15.0
Maximum	13.1	870	6.77	180	66.0
Mean	5.6	122	3.90	87	40.6
Standard Deviation	2.96	221	1.16	26	13.1

$$^* \text{Mean} = \frac{1}{n} \sum_{i=1}^n x_i$$

$$^{**} \text{Mean} = \frac{1}{n} \sum_{i=1}^n \ln(x_i) \quad \text{Note: } \frac{1}{n} \sum_{i=1}^n \ln(x_i) \neq \ln\left(\frac{1}{n} \sum_{i=1}^n x_i\right)$$

RVP = Reid Vapor Pressure (psia)

ST = Separator Temperature (°F)

SP = Separator Pressure (psia)

APIG = API Gravity (°API)