

**A Review of the Emission Estimates used by the
American Petroleum Institute
and the Synthetic Organic Compounds Manufacturing
Industry for Volatile Organic Compounds:
Theory and Application**

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ABSTRACT

This report reviews and critiques methods which are published by the United States Environmental Protection Agency, and also recommended by CONCAWE, for estimating evaporative losses from petrochemical storage tanks and industrial process plant. Areas for improvement and further study work are also proposed.

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EXECUTIVE SUMMARY

This Report investigates the calculations published by the United States Environmental Protection Agency for estimating gas losses from oil refinery process equipment and storage tanks.

The investigation includes the theory behind the calculations, the experiments carried out, and the data analysis techniques used to generate the final equations.

The calculations for storage tanks were found to be generally based on sound theory and good experiment. The small number of experiments carried out on external floating-roof tanks was a cause for concern, as was the assumption that internal floating-roof tanks were unaffected by wind.

The refinery equipment equations were less amenable to dissection than the those for storage tanks. The statistical approach to equipment failure and leakage is sound. However, a limited number of data were collected; given the large number of different designs and conditions of equipment likely to be operating on a given plant, the accuracy of the final estimates may be suspect.

Since this Report was completed, new versions of the equations for estimating losses from floating-roof storage tanks have been published [22]. From an initial consideration it appears that some of the concerns expressed in this Report about the experiments on external floating-roof storage tanks and also the effect of wind on internal floating-roof tanks have been addressed. However, it has been decided to publish this Report as it stands, since many of the issues discussed remain of scientific concern.

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1 INTRODUCTION

This Report is concerned with the theory and application of the estimates of emissions from storage tanks and process equipment (valves, pumps, etc.), as they have been presented by the United States Environmental Protection Agency (US EPA) and the American Petroleum Institute (API). It looks into possible inaccuracies in the calculations used for estimating gaseous emissions from these two aspects of the petrochemical industry. While some comment as to the validity of the presented theories is offered, no attempt at this stage has been made to develop an alternative theory or practice. As far as practicable, the sources of emissions have been quantified and their associated uncertainties ranked. However, there are limited data for an exercise of this sort.

Section 2 covers emissions from storage tanks, Section 3 covers the refinery equipment estimates.

1.1 SOURCES OF INACCURACY IN THE EMISSIONS EQUATIONS

There are several stages in the generation of an estimate of the emissions from a piece of equipment - and errors/inaccuracies are possible at each of these stages. Broadly, the process can be divided into a number of major steps. First comes the development of the estimating equations and emission factors to be used. Secondly, measurements are done in the field and entered into these correlations to generate emission estimates.

The stages in the development of the emissions factors can be broken down as follows:

- Develop theoretical model for emissions
- Perform experimental tests on equipment
- Develop correlations for emissions

During the development stage, there may be some simplification of the correlations

to ensure that fewer categories of emission source are used and that the data to be input are therefore more easily manipulable. In addition, the correlations may be recast in a form which is relevant to the most commonly used measurement quantities.

An assessment of the emissions from a piece of equipment using the factors and correlations can be broken down into two stages:

- Carry out field measurements on equipment and meteorology
- Use judgment when factors are not applicable or data cannot be measured

Each of the above stages has potential for introducing errors into the final estimate of emissions.

This Report concentrates on the steps in the development of the estimating equations. These stages are discussed in the next Sections.

2 EMISSIONS FROM STORAGE TANKS

This Section discusses the calculations developed by API for the estimating of emissions of volatile organic compounds (VOCs) from storage tanks. Emissions from fixed roof tanks, external floating-roof tanks and internal floating-roof tanks are covered. Section 2.4 contains a brief investigation into the effects of averaging parameters, such as wind speed and solar radiation, that have a nonlinear impact on the total emissions. This investigation is carried out for a typical external floating-roof tank. Section 2.5 contains example calculations for typical fixed and floating-roof tanks.

2.1 LOSSES FROM FIXED ROOF TANKS

The total loss from a fixed roof tank is the sum of the standing storage loss and the working loss. The standing storage loss is that associated with the tank contents evaporating during a daily cycle of heating and cooling. The working loss is associated with vapour expulsion while the tank is being filled and emptied. Equations for calculating these losses are presented in the United States Environmental Protection Agency's AP-42 [1]. The equations and the assumptions in their development are presented below.

2.1.1 Standing Storage Losses

Standing storage loss, or breathing loss, is caused by vapour expansion and contraction during a daily cycle of heating and cooling [2]. Figure 1 shows a schematic of the vapour space expansion caused by tank heating.

The tank is modelled as a fixed volume structure, containing liquid and vapour. The vapour space is sealed from the atmosphere by a vent (pressure/vacuum vent) that enables exchange only when the gauge pressure inside the tank falls below a certain specified pressure (air enters the tank) or rises above a certain specified pressure (vapour is emitted from the tank).

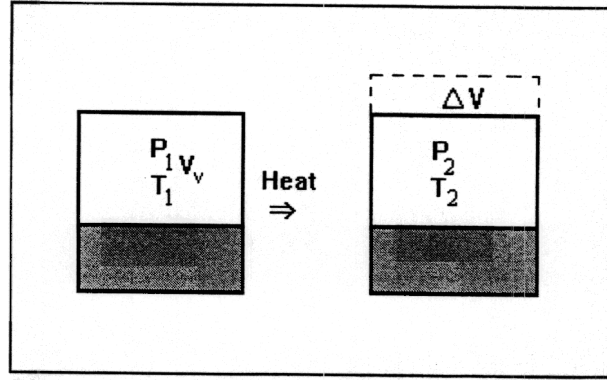


Figure 1: Tank Vapour Volume Expansion

The daily thermal breathing cycle is considered to proceed as follows [2]:

- i) The gas mixture is heated from its minimum condition to its maximum condition, and cools back to its minimum condition.
- ii) The increase in temperature causes the gauge pressure in the tank to exceed the pressure setting of the pressure/vacuum vent, and therefore vapour is vented.
- iii) As the gas mixture cools, the gauge pressure falls below the vacuum setting of the pressure/vacuum vent and air is admitted to the tank.

Analysis of this cyclical heating and cooling process led to the following equation for the standing storage loss [1]:

$$L_s = 365 V_v W_v K_E K_S$$

The number 365 arises from the annualisation of the emissions from the daily results.

V_v is the vapour space volume - ie it is the volume of the tank minus the volume of liquid in the tank [1]. It is the total volume of vapour at the lowest temperature in the day [2] - expressed in m^3 .

W_v is the density of vapour at the temperature at the surface of the liquid in the tank [1]; this temperature is taken as the average liquid surface temperature over the daily cycle for calculation purposes - expressed in $kg.m^{-3}$.

K_E is the vapour space expansion factor - it relates the volume of the vapour space to the volume of the vapour emitted over a daily cycle [2] - expressed as a dimensionless factor. Using the notation of Figure 1:

$$K_E = \Delta V / V_v \quad (1.2)$$

K_S is the vented vapour saturation factor - it is the molar density of vapour in the vented gas divided by the molar density of the vapour at the surface of the liquid [2] - expressed as a dimensionless factor.

Combining the four above variables gives the volume of the vented vapour multiplied by the density of this vapour, over a single daily cycle of heating and cooling. Multiplying this daily value by 365 gives the yearly figure for the tank emissions. It should be noted that the definition of K_E covers the fact that heating and cooling takes place over a 24-hour period.

The four factors in the standing storage loss equation are discussed below. The equations are presented in full, where appropriate. There is often a separation between the assumptions used to generate the original equation and those used to decide the inputs to that equation.

i) Tank Vapour Space Volume

The tank vapour-space volume, V_v , is the total volume of the tank less the volume of the liquid in the tank [1]. Geometrical allowance is made for the volume of the roof of cone- and dome-roofed tanks. Given a known tank geometry, the only unknown is the liquid height in the tank. No allowance is made for any tank internals.

For horizontal tanks, the assumption is made that the tank is half full of liquid [1]. It is acknowledged that this gives only an approximate value for emissions from horizontal storage tanks. For underground horizontal tanks, the assumption is that no breathing or standing storage losses occur because the insulating nature of the earth limits the diurnal temperature change [1].

ii) Vapour Density of Volatile Species

The density of vapour, W_v , is calculated using the following equation [1]:

$$W_v = \frac{M_v P_{vA}}{RT_{LA}} \quad (1.3)$$

where:

W_v = vapour density, kg/m³

M_v = vapour molecular weight, kg/kmol;

R = the ideal gas constant, 8315 J.kmol⁻¹K⁻¹;

P_{vA} = vapour pressure at daily average liquid surface temperature, Nm⁻²;

T_{LA} = daily average liquid surface temperature, K;

Some of the data required to determine the vapour density can be obtained by simplification and approximation. The notes given in AP-42 are described below.

The molecular weight of the vapour, M_v , can be found from tables provided in AP-42, or by analysing vapour samples. Where mixtures of organic liquids are stored in a tank, M_v can be calculated from the liquid composition [1]. The molecular weight of the vapour, M_v , is equal to the sum of the molecular weight, M_i , multiplied by the vapour mole fraction, y_i , for each component. The vapour mole fraction is equal to the partial pressure of component i divided by the total vapour pressure. For an ideal liquid mixture, the partial pressure of component i is equal to the true vapour pressure of component i (P) multiplied by the liquid mole fraction, (x_i). Therefore,

$$M_V = \sum M_i y_i = \sum M_i \left(\frac{P_{x_i}}{P_{VA}} \right)$$

where P_{VA} , total vapour pressure of the stored liquid, by Raoult's law, is:

$$P_{VA} = \sum P_{x_i}$$

The equations used to calculate the vapour density were tested by Radian in a report for the API [3]. They tested a variety of crude oils, aviation fuel and fuel oil. Their conclusions were that Raoult's Law gave an accurate vapour concentration based on measured liquid concentration for the crude oils and the refined products.

The true vapour pressure is the equilibrium partial pressure exerted by a volatile organic liquid [1]. AP - 42 provides figures and tables for calculating the vapour pressure of various petroleum liquids and chemicals. Alternatively, true vapour pressure for selected petroleum liquid stocks, at the stored liquid surface temperature, can be determined using the following equation [1]:

$$P_{VA} = \exp [A - (B/T_{LA})] \quad (1.6)$$

where: A = constant in the vapour pressure equation, dimensionless
 B = constant in the vapour pressure equation, K
 T_{LA} = daily average liquid surface temperature, K
 P_{VA} = true vapour pressure, Nm^{-2}

The true vapour pressure of organic liquids at the stored liquid temperature can be estimated by Antoine's equation [1]:

$$\log_e P_{VA} = A - \frac{B}{T_{LA} + C}$$

where: A, B, C = constants in vapour pressure equation
 T_{LA} = daily average liquid surface temperature, now expressed in $^{\circ}C$
 P_{VA} = vapour pressure at average liquid surface temperature, expressed as mm Hg

Equation 1.6 is a special case of Antoine's equation, with the units changed and $C = 0^{\circ}C$. (Note A , B & C are not numerically the same in equations 1.6 and 1.7 because the units have been changed).

If the daily average liquid surface temperature, T_{LA} , is unknown, the following equation is recommended [1]:

$$T_{LA} = 0.44T_{AA} + 0.56T_B + 3.87 \times 10^{-4} \alpha I \quad (1.8)$$

where: T_{LA} = daily average liquid surface temperature, °C
 T_{AA} = daily average ambient temperature, °C;
 T_B = liquid bulk temperature, °C;
 α = tank paint solar absorptance, dimensionless;
 I = daily total solar insolation factor, kJ.m⁻²;

AP-42 states that Equation 1.8 should not be used to estimate liquid surface temperature from insulated tanks. In this case, the average liquid surface temperature should be based on liquid surface temperature measurements from the tank.

Equation 1.8 was developed from a heat transfer model of the solar heating of the tank and several simplifying assumptions. The major assumptions used in the development of the heat transfer model were [2]:

- The gas space is fully mixed (uniform temperature and composition)
- The liquid space is fully mixed and remains at a constant temperature for the whole daily cycle.
- The tank wall can be characterised by three separate sections: the roof, the wall facing the sun, and the wall facing away from the sun. Each of the three elements can be characterised by a single temperature that varies throughout the daily cycle.
- Effects of rain and snow are neglected by the model.
- Heat capacities of the walls, roof and gas space are neglected.

The above five assumptions were used to generate equations for the gas space temperature in the tank based on the incident solar radiation (insolation) and the heat exchanged with the air surrounding the tank. The calculations for the heat input from insolation were taken from Duffie and Beckman [4]. The analysis is simplified further by assuming that the tank has a flat roof, and that the heat transfer coefficients to and from the outer surfaces of the tank are all equal. The heat transfer coefficients to and from the inner surfaces of the tank and between the gas and liquid in the tank are also assumed to be all equal [2].

Having developed an equation for the gas space temperature, the following conditions are assumed for simplification [2]:

- The ground reflectivity is 0.1 (dimensionless)
- The tank is situated at 35° North and at 610 m (2000 ft) altitude
- The day is April 15 (day number 105)

These parameters are assumed to represent "typical" conditions.

The liquid surface temperature variation is related to the daily gas space temperature variation by heat transfer considerations, assuming the liquid in the tank behaves as

a solid mass [2].

Heat transfer considerations are then used to relate the liquid surface temperature to the gas space temperature and the liquid bulk temperature. This analysis leads to Equation 1.8 above.

The daily average ambient temperature, T_{AA} , is calculated by assuming that daily temperature profile is sinusoidal, with the maximum temperature occurring two hours after solar noon [2].

If measurements are unavailable, the liquid bulk temperature, T_B , is calculated using the following equation [1]:

$$T_B = T_{AA} + 0.55(6\alpha - 1) \quad (1.9)$$

where: T_B = liquid bulk temperature, K
 T_{AA} = daily average ambient temperature, K
 α = tank paint solar absorptance, dimensionless;

It is assumed that the temperature of liquid in a white tank ($\alpha = 0.17$) is the same as the ambient temperature [2]. The difference between the bulk liquid temperature and the ambient temperature is assumed to vary linearly with absorptance [2].

A theoretical analysis of the effects of solar radiation on the tank is very complex [2]. Two of the starting assumptions of the US methods, however, appear invalid: the assumption that the gas space is uniformly mixed, and the assumption that the liquid is at a uniform, unchanging temperature throughout the day.

The first assumption probably does not have a large impact on the resulting equations, but the second assumption is clearly unreasonable. Woods et al [5] report a study that showed that the temperature difference between the liquid surface and the bulk liquid in a tank exposed to solar radiation could be up to 15°C. The bulk liquid would also be above its average temperature at the hottest part of the day.

Following the primary analysis, a second analysis considering the heat transfer through the liquid was used to generate a liquid surface temperature different to the bulk liquid temperature [2]. This analysis assumed that the liquid transferred heat as though it was a solid body; the result for the temperature difference appears to significantly underestimate the surface temperature.

A further assumption is that the average yearly bulk liquid temperature in a white tank is equal to the average yearly ambient temperature. This assumption would underestimate the temperature in summer, and, since there is no reason to suppose that the temperature is below ambient in winter, this must therefore underestimate the temperature. An underestimate of the surface temperature of the liquid, on which the vapour pressure is based, would lead to an underestimate of the evaporative losses from the tank.

iii) Vapour Space Expansion Factor

The vapour space expansion factor, K_E , is calculated using the following equation [1]:

$$K_E = \frac{\Delta T_V}{T_{LA}} + \frac{\Delta P_V - \Delta P_B}{P_A - P_{VA}} \quad (1.10)$$

where: ΔT_V = daily vapour temperature range, K;
 ΔP_V = daily vapour pressure range, Nm^{-2} ;
 ΔP_B = breather vent pressure setting range, Nm^{-2} ;
 T_{LA} = daily average liquid surface temperature, K;
 P_A = atmospheric pressure, Nm^{-2} ;
 P_{VA} = vapour pressure at daily average liquid surface temperature, Nm^{-2} ;

Equation 1.10 was developed by assuming the vapour behaves as an ideal gas, and that the total number of moles of air in the air/vapour mixture remains unchanged throughout the vapour expansion [2]. The tank is assumed to be equipped with a vent that ensures that the internal gas pressure differs from the outside atmospheric pressure by the vent pressure setting [2]. It is also assumed that the tank internal pressure is below atmospheric pressure at the minimum conditions (coldest part of the day) and above atmospheric pressure at the hottest part of the day [2].

The analysis follows a single daily (24-hour) cycle of heating and cooling, from the minimum to the maximum condition and back to the minimum condition. It is assumed that the temperature, pressure and volume are simultaneously at their maximum values at the maximum condition and are simultaneously at their minimum values at the minimum condition [2].

These assumptions lead to the equation [2]:

$$K_E = \frac{\Delta T_V}{T_{V1}} + \frac{\Delta P_V - \Delta P_B}{P_A + P_{BP} - P_{V2}} \quad (1.11)$$

where: ΔT_V = daily vapour temperature range, K;
 T_{V1} = minimum vapour temperature, K;
 ΔP_V = daily vapour pressure range, Nm^{-2} ;
 ΔP_B = breather vent pressure setting range, Nm^{-2} ;
 P_A = atmospheric pressure, Nm^{-2} ;
 P_{BP} = breather vent pressure setting, Nm^{-2} ;
 P_{V2} = maximum vapour pressure, Nm^{-2} ;

The following assumptions are made to convert Equation 1.11 into Equation 1.10 [2]. These assumptions are made for ease of calculation [2].

1. Since P_{BP} is small compared to P_A (typically 0.21kNm^{-2} compared to 101kNm^{-2}), it is neglected [2].
2. The minimum vapour space temperature, T_{V1} , is assumed to be negligibly different from the daily average liquid surface temperature, T_{LA} [2].

3. Low vapour pressure stocks have a vapour pressure small compared to atmospheric pressure [2]. The minimum vapour pressure, P_{v2} , may be replaced with the vapour pressure at the average liquid temperature, P_{vA} , with little loss of accuracy [2].

Further assumptions and simplifications are made to generate the inputs for Equation 1.10:

1. The daily vapour temperature range ΔT_v , is calculated using the following equation:

$$\Delta T_v = 0.72 \Delta T_A + 1.37 \times 10^{-3} \alpha I \quad (1.12)$$

where: ΔT_A = daily ambient temperature range, K;
 α = tank paint solar absorptance, dimensionless;
 I = daily total solar insolation factor, kJ.m^{-2} ;

This is again assuming "typical" solar radiation parameters.

2. The daily vapour pressure range, ΔP_v , can be calculated using the following equation [1]:

$$\Delta P_v = P_{vX} - P_{vN} \quad (1.13)$$

where:

P_{vX} = vapour pressure at the daily maximum liquid surface temperature, Nm^{-2} ;
 P_{vN} = vapour pressure at the daily minimum liquid surface temperature, Nm^{-2} ;

The following method can be used as an alternative means of calculating ΔP_v for petroleum liquids (from Equation 1.6):

$$\Delta P_v = \frac{0.50 B P_{vA} \Delta T_v}{T_{LA}^2} \quad (1.14)$$

where: ΔP_v = daily vapour pressure range, Nm^{-2}
 B = constant in the vapour pressure equation, K;
 P_{vA} = vapour pressure at the daily average liquid surface temperature, Nm^{-2} ;
 ΔT_v = daily vapour temperature range, K;
 T_{LA} = daily average liquid surface temperature, K;

This assumes that the daily vapour space temperature change is twice the daily liquid temperature change [2]. This assumption was developed by a combination of theory and experiment.

3. The breather vent pressure setting range, ΔP_B , is calculated using the following equation [1]:

$$\Delta P_B = P_{BP} - P_{BV} \quad (1.15)$$

where: P_{BP} = breather vent pressure setting, Nm^{-2}
 P_{BV} = breather vent vacuum setting, Nm^{-2}

If specific information on the breather vent pressure setting and vacuum setting is not available, 0.21 kNm^{-2} for P_{BP} and -0.21 kNm^{-2} for P_{BV} are used. If the tank is bolted or rivetted and the roof or shell plates are not vapour tight, ΔP_B is assumed to be zero, even if a breather vent is used. The estimating equations for fixed roof tanks do not apply to either low or high pressure tanks: if the breather vent pressure or vacuum setting exceeds 6.9 kNm^{-2} , the calculated standing storage losses could potentially be negative [1].

iv) Vented Vapour Saturation Factor

The vented vapour saturation factor, K_s , is calculated using the following equation [1]:

$$K_s = \frac{1}{1 + 0.025 P_{VA} H_{VO}} \quad (1.16)$$

where: K_s = vented vapour saturation factor, dimensionless
 P_{VA} = vapour pressure at daily average liquid surface temperature, Nm^{-2} ;
 H_{VO} = vapour space outage, m.

This vapour space outage is the volume of the vapour space divided by the area of the liquid surface in the tank. For flat-roofed tanks, it is simply the height of the tank minus the height of the liquid in the tank.

Air is admitted into the tank at the minimum condition. Stock vapour evaporates into this unsaturated mixture of vapour and air [2]. The gas at the liquid surface is assumed to be saturated with vapour [2]. The concentration of the vented vapour is different from the concentration of the vapour at the liquid surface; it depends on the rate at which the vented vapour is replaced by newly evaporated stock [2].

By assuming the number of moles of vapour evaporating each day is constant, the number of moles of vapour in the vented gas may be equated to the number of moles of vapour evaporated from the stock liquid [2]. This can be expressed mathematically as:

$$\rho_G \Delta V y_v = K A_L t_D (y_v^o - y_v) \quad (1.17)$$

where: ρ_G = molar density of vented gas;
 ΔV = volume of vented gas;
 y_v = mole fraction of vapour in vented gas;

K = overall mass transfer coefficient between liquid surface and vented gas;
 A_L = surface area of liquid;
 t_D = length of a daylight hours;
 y_v° = mole fraction of vapour at liquid surface (= saturated vapour pressure at liquid surface temperature).

As stated earlier, K_s relates the mole fraction of vapour in the vented gas to the mole fraction of vapour in the gas at the liquid surface, that is $K_s = y_v / y_v^\circ$. This means that when $K_s=1$ the vented gas is saturated; when $K_s=0$ there is no vapour in the vented gas [2].

Equation 1.17 can be rearranged to give an expression for K_s [2]:

$$K_s = \frac{1}{1 + \left(\frac{P_A H_{vo} \Delta T_v}{R t_D K T_{LA}^2} \right) \left[1 + \left(\frac{0.50B}{T_{LA}} \right) \left(\frac{\frac{P_{VA}}{P_A}}{1 - \frac{P_{VA}}{P_A}} \right) \right]} \quad (1.18)$$

Here B is a constant in the simplified vapour pressure expression (Equation 1.6); the other variables and constants are as before.

As the vapour space decreases, K_s increases; as the vapour pressure increases, K_s decreases [2]. Both are physically reasonable.

From this equation, however, there is insufficient information to work out the overall mass transfer coefficient K [2]. Instead an analytical expression was used to develop a correlation for K_s [2]. In this, the liquid surface temperature, the mass transfer coefficient, the vapour pressure constant and the vapour temperature difference were assumed to be constant for all situations. Correlations were then developed which are expressed in the form presented in Equation 1.16 above. It should be noted, however, that this is not mathematically equivalent to the form in Equation 1.18, even assuming the constancy of the above parameters.

Three sets of data were used to develop the detailed correlations. They were obtained from the Western Oil and Gas Association [6], the US Environmental Protection Agency [7], and the American Petroleum Institute [8]. Of these tests, 10 API tests, 12 of 15 EPA tests and 21 of 44 WOGA tests were used in the development of the correlation. A least-squares linear regression fit was used on the data [2].

2.1.2 Working losses

The working losses are estimated from the following equation [1]:

$$L_w = 4.13 \times 10^{-4} M_v P_{VA} Q K_N K_P \quad (1.19)$$

where: L_w = yearly working losses, kg;
 M_v = vapour molecular weight, kg/kmol;

- P_{VA} = vapour pressure at daily average liquid surface temperature, Nm^{-2} ;
 Q = annual net throughput, m^3 ;
 K_N = turnover factor, dimensionless;
 for turnovers > 36 , $K_N = (180 + N)/6N$
 for turnovers ≤ 36 , $K_N = 1$
 K_P = working loss product factor, dimensionless

The number of turnovers per year is the annual throughput divided by the tank maximum liquid volume. $K_P = 0.75$ for crude oils. For all other organic liquids, $K_P = 1$.

This equation can be broken down into its constituent parts. It represents the mass of the vapour that is expelled each time the tank is filled, multiplied by the number of times the tank is filled, multiplied by two other factors. The vapour is assumed to be saturated. The factor K_N is used to account for the fact that the tank vapour space may not have reached saturation before the tank is refilled. It is assumed that the tank, however large, takes ten days to reach saturation, and will thus be saturated for each filling if it is filled 36 times or less. The working loss product factor, K_P , accounts for the fact that crude oil takes more time to reach saturation, due to limitations which arise from the time taken for equilibration and mass transfer in the liquid phase.

2.1.3 Summary of Fixed-roof-tank Emission Estimates

The equations for estimating standing storage losses are based on a combination of sound theory and correlation developed by many experiments. The model of the tank and the use of heat and mass transfer theory with some simplifications coupled with a pragmatic approach to developing an empirical correlation with some basis in theory appear to lead to good quality estimating calculations. The major causes for concern are the simplifications introduced in the heat transfer model and the averaging of the meteorological data. Both these points apply to all types of storage tanks and will therefore be dealt with in detail in the general conclusions in Section 4. At this stage it would appear that there is room for improvements to the theory and for further experiments in this area.

Since the fixed roof tank is unable to compensate for the rising liquid level as it is being filled, one would expect the working loss to form a significant proportion of the total loss. The equation for working loss is by necessity an average equation, since the actual cycle of filling and emptying over the year cannot be considered for each tank. The figure of ten days for the tank to reach saturation does not consider the tank size or the nature of the liquid being stored. The introduction of the crude oil factor is a clear oversimplification; given that UK crude oils are generally lighter than US crude oils, it may not be as applicable for UK calculations.

2.2 LOSSES FROM EXTERNAL FLOATING-ROOF TANKS

The equations presented below, from AP-42 [1], were developed to apply to external floating-roof tanks and specifically exclude the following applications [1]:

- 1 Estimating losses from unstable or boiling stocks, or from mixtures of hydrocarbons or petrochemicals for which the vapour pressure is not known or cannot readily be predicted;

- 2 Estimating losses from tanks in which the materials used in the rim seal and/or roof fittings are either deteriorated or significantly permeated by the stored liquid.

Total external floating-roof tank emissions are the sum of rim seal, withdrawal, and roof fitting losses. Rim seal losses are associated with the edge of the floating roof, where it contacts the shell of the tank. Withdrawal losses are similar to the working losses for fixed roof tanks, though the mechanisms involved are different. Roof fitting losses are due to evaporation through fittings that penetrate the floating roof.

2.2.1 Rim-seal Losses

Rim seal losses from floating-roof tanks can be estimated using the following equation [1]:

$$L_R = K_R V^n P^* D M_v K_C$$

where: L_R = rim seal loss, kg
 K_R = seal factor, $\text{kmols} \cdot \text{m}^{-(n+1)}$
 V = average wind speed at tank site, ms^{-1}
 n = seal-related wind speed exponent, dimensionless;
 P^* = vapour pressure function, dimensionless;
 D = tank diameter, m
 M_v = average vapour molecular weight, kg/kmol;
 K_C = product factor.

The rim seal factors were developed by a series of experiments reported in 1970 [9].

If the wind speed at the tank site is unknown, either the wind speed at the nearest available weather station, or an average value from the tables presented in AP-42 should be used [1].

The dimensionless vapour pressure function is defined by

$$P^* = \frac{P_{vA}/P_A}{[1 + (1 - [P_{vA}/P_A]^{0.5})^2]}$$

where:

P_{vA} = vapour pressure at daily average liquid surface temperature, Nm^{-2} ,
 P_A = atmospheric pressure, Nm^{-2} ;

Experiments were carried out on mixtures of n-octane and propane to determine a correlation to relate the vapour pressure of the liquid to its emission rate [10]. Three correlations were tested, including that shown in Equation 2.2. The theoretical basis of these correlations was not discussed. The conclusion of the review was that the difference between three correlations was small compared with the scatter on the emission data [10]. However, it is noted that extrapolation to high vapour pressures

($>60 \text{ kNm}^{-2}$) is unwise.

It is noted in AP-42 that the API recommends using the stock liquid temperature to calculate P_{VA} for use in Equation 2.2 instead of the liquid surface temperature. If the stock liquid temperature is unknown, API recommends the following equations to estimate the stock temperature:

Tank Colour	Average Annual Stock Temperature, T_s (K)
White	$T_a + 0.0$
Aluminum	$T_a + 1.4$
Grey	$T_a + 1.9$
Black	$T_a + 2.8$

T_a is the average annual ambient temperature in Kelvin. Note that these figures come from Equation 1.9.

The product factor, K_C , is 0.4 for crude oils and 1.0 for all other organic liquids. API carried out tests on gasoline, octane/propane mixtures and crude oil [10]. Their findings were that differences in the emission rates for the first two liquids could be accounted for by differences in the true vapour pressure and the molecular weight of the products. However, tests on the crude oil showed that emissions predicted had to be multiplied by a factor of 0.4 to tally with the measured emissions. The reason given by the API for this factor is that the mass transfer of light components through the crude oil to the liquid surface is much slower than mass transfer through the gasoline or octane/propane mixtures. Tests carried out with pure hexane and octane showed that the emission factors developed for propane/octane mixtures predicted the measured emissions well [10]. This means that the octane/propane evaporation process is limited by the transfer from the liquid surface to the vapour phase, not by transfer to the liquid surface.

2.2.2 Withdrawal Losses

The withdrawal losses from floating-roof storage tanks can be estimated using Equation 2.3 below [1].

$$L_{WD} = \frac{QCW_L}{D} \tag{2.3}$$

where:

- L_{WD} = withdrawal loss, kg
- Q = annual throughput, m^3 , (tank capacity times number of annual turnovers)
- C = shell clingage factor, m^3/m^2 ;
- W_L = average organic liquid density, kg/m^3 ;
- D = tank diameter, m

Since the tank capacity is the tank cross sectional area multiplied by the tank height,

the throughput divided by the tank diameter can be expressed differently: it is the perimeter of the tank, multiplied by the tank height and the annual number of turnovers, divided by four. This makes the relationship in Equation 2.3 more transparent.

Clingage factors are provided in AP-42 for two products, crude oil and others, and three tank linings: light rust, dense rust and gunite lining.

The clingage factors were developed from a series of experiments [11]. These involved a temperature-controlled test tank with a test plate immersed in stock liquid. The test plate was raised out of the stock, past a vapour-mounted resilient-filled primary seal. Two seal configurations were tested: the first had no gap between the plate and the seal, the second had a small gap. In the former case, the stock liquid was wiped from the plate as it was raised.

The carbon-steel test plate was 0.3 m wide, and was raised and lowered over a range of 5.1 m. Two plates, one clean and one lightly rusted, were used. The plate was raised and lowered at a rate of 0.25 cm/s for at least 20 cycles, with the evaporative loss being measured by the decrease in the stock level in the test tank. Octane and a light crude oil were used as stock liquids.

The clingage factors do not consider the meteorological conditions or whether the tank has an external or internal floating-roof. This is clearly an oversimplification, but the significance of the working loss compared to the standing loss is small.

2.2.3 Roof-fitting Losses

The roof fitting losses from external floating-roof tanks can be estimated by the following equation [1]:

$$L_F = F_F P^* M_V K_C$$

where: L_F = the roof fitting loss, kg
 F_F = total roof fitting loss factor, kmol;
 P^* , M_V , K_C are as defined for Equation 2.1

$$F_F = [(N_{F1} K_{F1}) + (N_{F2} K_{F2}) + \dots + (N_{Fn} K_{Fn})]$$

where:

N_{Fi} = number of roof fittings of a particular type ($i = 0, 1, 2, \dots, n_i$), dimensionless
 K_{Fi} = roof fitting loss factor for a particular type fitting ($i = 0, 1, 2, \dots, n_i$), kmol;
 n_i = total number of different types of fittings, dimensionless

The value of F_F may be calculated by using actual tank-specific data for the number of each fitting type (N_{Fi}) and then multiplying by the fitting loss factor for each fitting (K_{Fi}).

The roof fitting loss factor, K_{Fi} for a particular type of fitting, can be estimated by the following equation:

$$K_F = K_{Fa} + K_{Fb} V^m \quad (2.6)$$

where:

- K_F = loss factor for a particular type of roof fitting, kmol
- K_{Fa} = loss factor for a particular type of roof fitting, kmol
- K_{Fb} = loss factor for a particular type of roof fitting, $\text{kmol s}^m \text{m}^{-m}$
- m = loss factor for a particular type of roof fitting, dimensionless
- V = average wind speed, ms^{-1}

The roof fitting loss factors were developed through a series of tests in a wind tunnel [12]. Four fittings were tested simultaneously in each test: slotted guide pole with well, covered well, roof drain and adjustable roof leg. Each fitting had its own reservoir; the loss from that fitting could be measured individually. These four fittings were assumed to be the most common fittings in current use [12]. Access hatches, gauge-float wells, gauge-hatch/sample wells, vacuum breakers and rim vents were assumed to behave as covered wells. A number of tests were carried out: the product in the test tank was either n-hexane or a mixture of propane and n-octane; the initial product level in the tank was varied; fittings were operated in various configurations (e.g. gasketed or ungasketed well-cover); measurements were taken at wind speeds of 0, 2.24 and 6.26 m/s (0, 5 and 14 mph). API developed fitting factors based on these tests [12].

A very limited amount of data was used to develop the correlations, with only two or three points being collected for each fitting at the tested wind speeds. Using these data to develop three fitting factors is highly suspect.

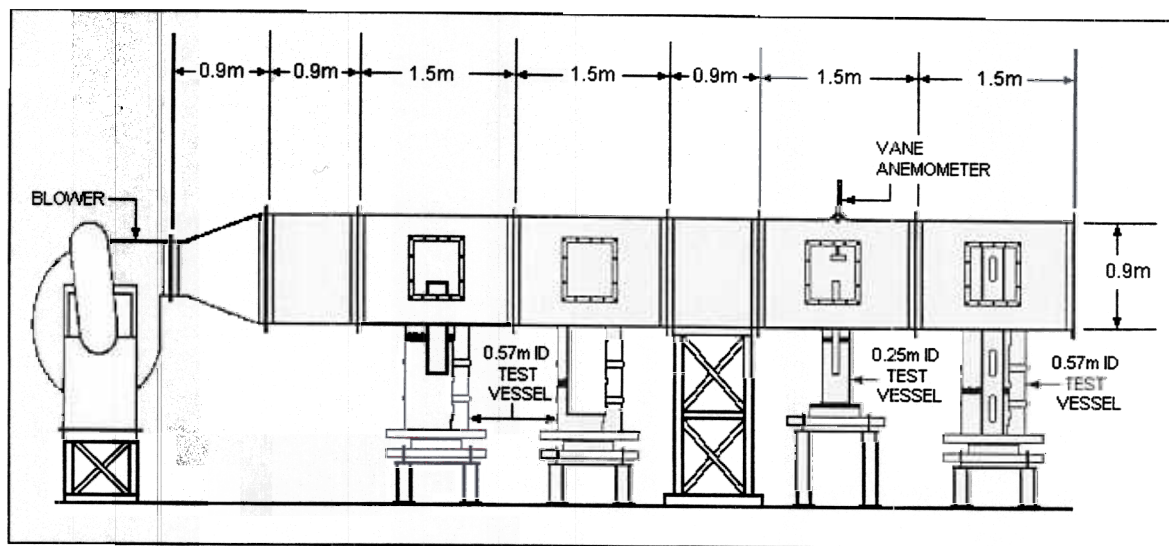


Figure 2: Wind Tunnel Test Facility

It is reported that the original wind tunnel wind speed measurements are 0.85 times those recorded by a pitot tube used for calibration [13]. With the factors often

varying as greater than the square of the wind speed, this casts doubt on the accuracy of the developed factors.

The fitting factors are shown to be heavily dependent on the wind speed over the fittings. The wind speed over the fitting may not be the same as the wind speed at the tank site, or indeed the wind speed at the nearest weather station, which is recommended as an alternative. API carried out a series of experiments to relate the wind speed at the local weather station to the wind speed at the tank surface, for various tank heights [14]. They developed two methods, which showed a 25-30% difference between them, but they did not develop a procedure for general use. The tank level had a significant impact on the wind speed over the roof surface: the wind speed first falls then rises as the tank roof is lowered.

Floating roofs typically have only certain types of roof fittings - for example access hatches. The number of other fittings, such as roof legs and roof drains, varies with the diameter of the tank and the roof construction. The API carried out a survey of three tank manufacturers to find out the typical numbers of roof legs, vacuum breakers and roof drains on a floating roof [12]. These typical figures are recommended for use in the absence of actual tank data [1].

2.2.4 Summary of External Floating-roof-tank Estimates

Unlike the equations for estimating fixed roof losses, the equations for estimating losses from external floating-roof tanks are essentially empirical, with little recourse to theory.

The experiments carried out to determine the rim seal losses were published in the early seventies. The extent to which the design and maintenance of rim seals currently in use in the UK compare to those used for the experiments is uncertain. The idea that the losses are a simple power-law function of the wind speed also needs further investigation.

The withdrawal loss equation is based on clingage factors developed from simple experiments. Since the factors are independent of tank operation and meteorological conditions, this equation is unlikely to be highly accurate. However, the withdrawal losses tend to form a small fraction of the total losses from floating-roof tanks.

The deck fitting loss factors were developed from wind tunnel experiments. There were two notable flaws in the experimental design: firstly, the experimental procedure was so lengthy that few experiments could be carried out; secondly, it was assumed that some untested components behaved as others for which experiments had been done. The first problem means that several of the correlations were fitted to tiny numbers of points, with no repeat experiments carried out. The second problem was highlighted in the May 1994 addendum to the API external floating-roof publication [13], which affected the results greatly. Both problems leave open the possibility of inaccuracy in the emission estimates.

The vapour pressure function is used as a measure of the volatility of the stored liquid. The experiments reported [10] do not give overwhelming justification to this function. This is an area that might benefit from further study, since the vapour pressure function forms the basis of many of the estimation equations.

2.3 LOSSES FROM INTERNAL FLOATING-ROOF TANKS

The equations provided in AP-42 [1] apply only to freely vented internal floating-roof tanks. They are not intended to estimate losses from closed internal floating-roof tanks (tanks vented only through a pressure/vacuum vent).

Total internal floating-roof tank emissions are the sum of rim seal, withdrawal, deck fitting, and deck seam losses. These losses are similar to their equivalents for external floating-roof tanks, although the mechanisms are different.

2.3.1 Rim-seal Losses

Rim seal losses from floating-roof tanks can be estimated by the following equation [1]:

$$L_R = K_R P^* D M_v K_C \quad (3.1)$$

where:

- L_R = rim seal loss, kg;
- K_R = seal factor, kmol/m; see below;
- P^* = vapour pressure function, dimensionless; see Note 4 to Equation 2.1;
- D = tank diameter, m
- M_v = average vapour molecular weight, kg/kmol; see Note 1 to Equation 1.3;
- K_C = product factor; as defined for Equation 2.1.

The rim seal factors were developed by a series of experiments on various tank configurations in a 6.1 m (20ft) diameter test rig (see Figure 3) [10]. The rim seal factors were obtained by subtracting the emissions due to deck seams and deck fittings from the total losses.

The three tank configurations tested were:

Bolted, non-contact deck with access hatch, column well and vacuum breaker. Fitted with a vapour-mounted flexible wiper primary seal and a flexible wiper secondary seal.

Welded, contact deck with guide pole, bleeder vent, column well and bolted access hatch. Fitted with a liquid-mounted, resilient foam-filled primary seal and a flexible wiper secondary seal.

Bolted, contact deck with a column well. Fitted with a vapour-mounted, resilient foam-filled primary seal and a resilient foam-filled secondary seal.

The hydrocarbon concentrations at inlet and outlet were monitored. The inlet air velocity, ambient conditions and the temperatures of the stock liquid and vapour were measured and controlled.

The seal gaps were varied, the roof height in the tank was varied and the product type and temperature were varied for the experiments. The air flow rate and temperature were also varied.

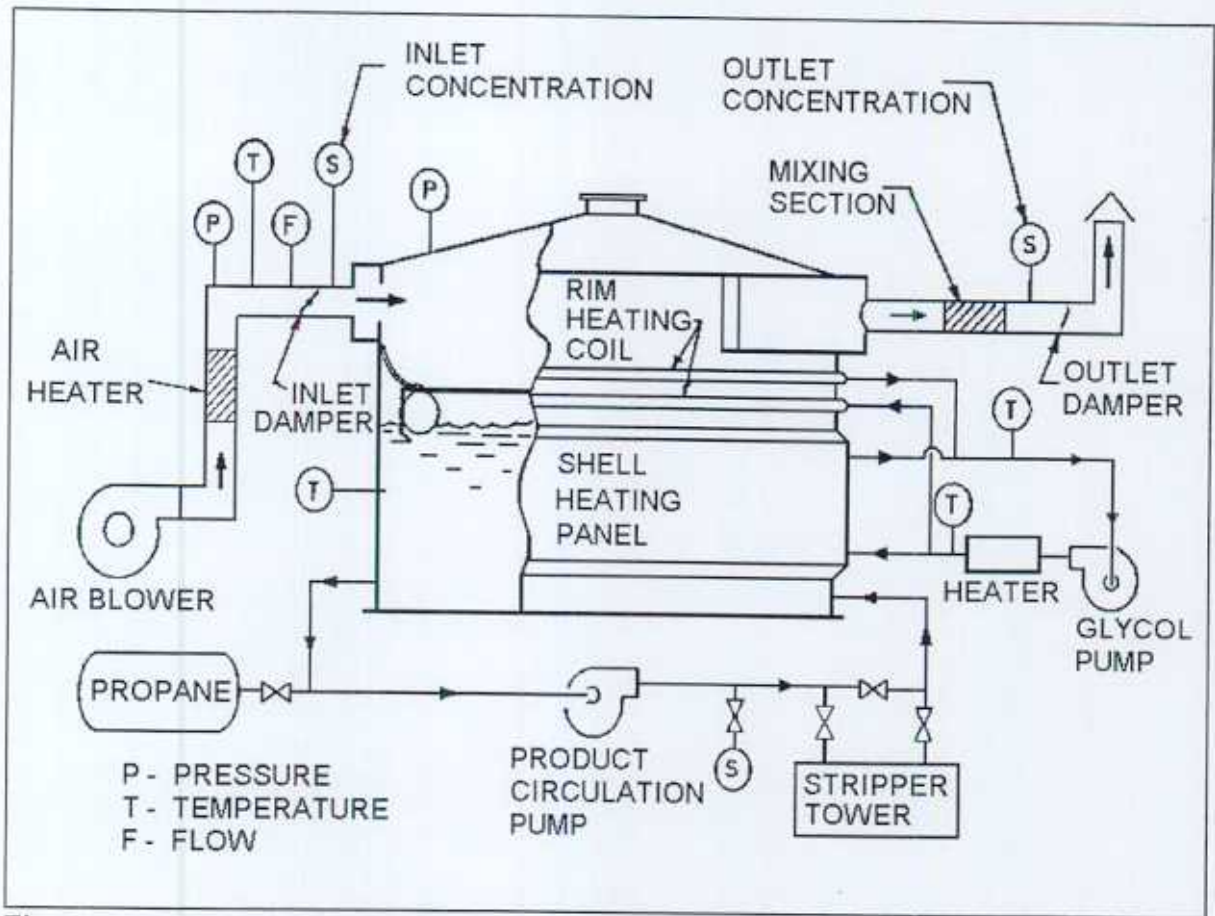


Figure 3: Internal Floating-Roof Test Rig

Initial tests were run with the test tanks sealed with polyurethane sheeting. The so-called residual losses when running under these conditions were apportioned, proportionally by area, between the seals and the deck fittings. It was assumed that the deck seams did not leak after sealing [10]. When the rim seals were sealed for subsequent experiments, the rim seal losses were assumed to be equal to these residual values.

The deck seam loss for bolted decks was found by measuring the emissions with and without the deck seams taped and taking the difference.

The tanks were then tested with the rim-seals sealed and taped, but the deck seams and the deck fittings untaped. The loss from the deck fittings could then be calculated by subtracting the loss from the deck seams and the residual loss from the rim seals from the measured total loss in this mode.

Adding the loss from the deck fittings to the loss from the deck seams gave the total loss from the deck. Subtracting the deck loss from the total loss, when none of the deck was sealed, gave the loss from the rim seal system.

Four rim-seal configurations were tested: vapour-mounted primary seals, with and without secondary seals, liquid-mounted primary seals, with and without secondary seals.

Having determined average values for rim seal losses for the four configurations, they were converted to loss factors by assuming that the rim seal loss was a linear

function of the tank diameter (reasonable since it relates to the tank perimeter) and the vapour pressure function, P^* [10].

API define a "tight" seal as one that has a gap of less than 3.18 mm (1/8 inch) at all parts of the rim at all heights in the tank [10]. AP-42 does not show the factors for tight seals, presumably on the assumption that a tight seal is unachievable in practice.

2.3.2 Withdrawal Losses

The withdrawal loss from internal floating-roof storage tanks can be estimated using Equation 3.2:

$$L_{WD} = \frac{QCW_L}{D} \left[1 + \left(\frac{N_C F_C}{D} \right) \right] \quad (3.2)$$

where:

N_C = number of columns, dimensionless;
 F_C = effective column diameter, m (column perimeter [m]/ π);
 L_{WD} , Q , C , W_L , and D are as defined for Equation 2.3.

AP-42 provides typical figures for number of columns and for effective column diameter, if the details for a specific tank are not known.

2.3.3 Deck-fitting Losses

Fitting losses from internal floating-roof tanks can be estimated by the following equation [1]:

$$L_F = F_F P^* M_V K_C \quad (3.3)$$

where:

F_F = total deck fitting loss factor, kmol
 $= [(N_{F1} K_{F1}) + (N_{F2} K_{F2}) \dots + (N_{Fn} K_{Fn})]$

where:

N_{Fi} = number of deck fittings of a particular type ($i = 0, 1, 2, \dots, n_i$), dimensionless;
 K_{Fi} = deck fitting loss factor for a particular type fitting, kmol;
 n_f = total number of different types of fittings
 P^* , M_V , and K_C are as defined in Equations 2.1 and 2.2.

Where tank-specific data for the number and kind of deck fittings are unavailable, then F_F can be approximated according to tank diameter [1]. AP-42 plots F_F against tank diameter for column-supported fixed roofs and self-supported fixed roofs.

The losses from individual fittings were measured for the test tank [10]. The losses from some fittings were determined directly; some fittings were found by subtraction and some by assuming the fitting behaved similarly to a tested fitting.

The measured losses in the test tank were scaled to what was believed to be the size of a typical fitting. This scaling was done linearly, on the assumption that the losses from long, narrow fittings would be proportional to the perimeter of the fitting [10].

Recognising the inaccuracies of their analysis, the API recommend rounding the deck fitting factors to two significant figures. This is how they appear in AP-42.

The findings of Woods et al [5] seem to indicate that the losses from internal floating-roof tanks vary with wind speed. Experiments carried out to determine the loss factors for internal floating-roof tanks did explore the effect of varying the wind speed; the conclusion was that the effect of the wind was not significant below 8.9 m/s (20 mph) [10].

2.3.4 Deck-seam Losses

Deck seam loss can be estimated by the following equation [1]:

$$L_D = K_D S_D D^2 P^* M_V K_C \quad (3.4)$$

where:

$$\begin{aligned} K_D &= \text{deck seam loss per unit seam length factor, kmol/m} \\ S_D &= \text{deck seam length factor, m/m}^2 \\ &= L_{\text{seam}} / A_{\text{deck}} \end{aligned}$$

$$\begin{aligned} \text{where: } L_{\text{seam}} &= \text{total length of deck seams, m} \\ A_{\text{deck}} &= \text{area of deck, m}^2 = \pi D^2 / 4 \\ D, P^*, M_V, \text{ and } K_C &\text{ are as defined for Equation 2.1.} \end{aligned}$$

As described above, deck seam losses were measured by taking the difference between emissions tests with all loss sources sealed and tests with all loss sources except the deck seams sealed. Only bolted decks were tested; it was assumed that no losses occur from properly welded decks [10].

It was assumed that the total losses were a linear function of the deck seam length and the vapour pressure function, P^* [10].

If the deck seam length is not known, the deck seam length factor can be approximated from the seal configuration and the roof area [1].

2.3.5 Summary of Internal Floating-roof-tank Estimates

As with external floating-roof tanks, the equations for internal floating-roof tanks were developed largely through experiment. The major difference is that a fast measuring system enabled many experiments to be carried out.

The rim seal, deck fitting and deck seam factors were all developed from the same series of experiments. These experiments were carried out recently and in large numbers. There is every reason to suppose that the fittings and rim seals tested conform to current practice, or are at least close to it, and the demonstrated repeatability of the experiments shows their precision. The decision to exclude the

effects of wind from the equations developed from the experiments is probably the biggest cause for concern.

As with the external floating-roof tanks, the volatility of the stored liquid is introduced into the equation as the vapour pressure function. This is again an area that could be further investigated.

The withdrawal equation is identical to that used for external floating-roof tanks, with an added term to cover clingage to the internal columns of the tank. There is no doubt that this is an oversimplification. However, it is less certain as to whether any major modifications would arise if the accuracy of this estimate were to be re-evaluated - either by experiment or modelling.

2.4 AVERAGING OF NONLINEAR PARAMETERS

This section takes the form of a short worked example. Some parameters in the estimating equations, such as wind speed and solar radiation, have a nonlinear relationship to the emission. The equations generally recommend average values to be used for these parameters. Using a typical tank as an example, the worked example examines the impact of this averaging on the overall result.

2.4.1 Example of an External Floating-roof-tank

An assumption is made in this example of a 6.1 m (20ft) diameter external floating-roof tank, 379 m³ (100000 US gallon) volume, with 10 turnovers per year. The tank is covered with light rust, with a white roof and white shell, both in good condition. The floating roof is a welded double deck, with a mechanical shoe primary seal and a shoe-mounted secondary seal. The deck has the following fittings:

One 25 cm (10-inch) diameter vacuum breaker, weighted, mechanically actuated, gasketed.

One unslotted guidepole, with ungasketed sliding cover.

Six 7.6 cm (3-inch) adjustable roof legs.

One 7.6 cm (3-inch) open roof drain.

One 15.2 cm (6-inch) rim vent, weighted, mechanically actuated, gasketed.

One 20 cm (8-inch) gauge hatch/sample well, weighted, mechanically actuated, gasketed.

One 51 cm (20-inch) diameter gauge float well, with ungasketed unbolted cover.

One 61 cm (24-inch) diameter access hatch, with gasketed bolted cover.

The tank is in Phoenix, Arizona, which has the following basic meteorological conditions:

Daily average ambient temperature = 21.8°C (71.2°F)

Annual average maximum temperature = 29.5°C (85.1°F)

Annual average minimum temperature = 14.1°C (57.3°F)

Average wind speed = 2.8 m/s (6.3 mph)

Annual average daily insolation = 21.2 MJ/m² (1869 BTU/ft²)

Contents of the tank, by mass: benzene 75%, toluene 15%, cyclohexane 10%

2.4.2 Monthly Averaging of Emissions

Firstly, the emissions calculated using the annual average values of wind speed and solar radiation were compared with the emissions calculated using the monthly average values. The bulk temperature was based on the annual average temperature in both cases.

		Emissions (in kg/year)	
		Yearly	Monthly
Benzene		580	598
Toluene		35	36
Cyclohexane		79	82
TOTAL		695	716

This represents a difference of 3.0% in the total emissions.

2.4.3 Effects of Wind-speed on Emissions

The total yearly emissions were calculated using wind speeds of 1.3 and 4.3 m/s (3.0 and 9.6 mph). Averaging these yearly emissions and comparing the result to the average yearly values using the wind speed of 2.8 m/s (6.3 mph) gives some idea of the impact of averaging the wind speed. It does not consider the effect of gusts of high wind, but since the equations were developed using a maximum wind speed of 6.3 m/s (14 mph), it is not reasonable to expect these equations to provide accurate estimates at high wind speeds.

	Speed (m/s)			
	2.8	1.3	4.3	(1.3 + 4.3)/2
Benzene	580	267	912	589
Toluene	35	16	54	35
Cyclohexane	79	37	125	81
TOTAL	695	319	1092	706

This represents a 1.6% difference in total emissions.

2.4.4 Ambient-temperature Effects on Emissions

In a similar way, ambient temperatures of 14.1°C and 29.5°C (57.3°F and 85.1°F) were used to calculate emissions.

	Ambient Temperature (°C)			
	21.8	14.1	29.5	(14.1 + 29.5)/2
Benzene	580	394	842	618
Toluene	35	23	53	38
Cyclohexane	79	54	115	84
TOTAL	695	471	1010	740

This represents a 6.6% difference in total emissions.

If one used a sinusoidal temperature profile to determine the emissions, it would differ from the average value by less than the above case. However, the effects of averaging solar radiation input have been neglected.

2.4.5 Summary of Non-linearity Effects

This initial study shows that the linearity of the emissions equations with respect to temperature and wind speed is such that using average values has only a small influence on the result. A more rigorous study, looking at the averaging used in the generation of the equations themselves would give further insight into the errors introduced by the averaging process.

2.5 RELATIVE SIGNIFICANCE OF FACTORS AFFECTING EMISSIONS

This section contains workings to illustrate some points made in earlier sections. The tanks and their fittings have been chosen to show the relationships between the storage and working losses for the three types of tank.

2.5.1 Example of a Fixed-roof Tank

It is assumed that a tank is 3.7 m (12ft) high with a diameter of 1.8 m (6ft). The average height of the liquid in the tank is 2.4 m (8ft), the maximum height of liquid

is 2.7 m (9ft). The tank working volume is 7.2 m^3 (1904 US gallons). With five tank turnovers per year, this gives an annual net throughput of 36.0 m^3 (9520 gallons/year). Both shell and roof are white, and the paint is in good condition. The roof is cone-shaped, with a height of 0.056m (0.185ft) and a slope of 0.06167 m/m. The vacuum and pressure breather vents are set to gauge pressures of -0.21 kNm^{-2} and $+0.21 \text{ kNm}^{-2}$ respectively.

The tank is located in Denver, Colorado, which has the following basic meteorological conditions:

Daily average ambient temperature = 10.2°C (50.3°F)

Annual average maximum temperature = 17.9°C (64.3°F)

Annual average minimum temperature = 2.3°C (36.2°F)

Average wind speed = 3.9 m.s^{-1} (8.7 mph)

Annual average daily insolation = 17.8 MJ.m^2 (1568 BTU/ft²)

Contents of the tank, by mass: benzene 89%, toluene 8%, cyclohexane 3%

The yearly losses are as follows:

Standing storage losses = 15.4 kg (34.11 lb)

Withdrawal losses = 7.24 kg (15.97 lb)

Total losses = 22.7 kg (50.07 lb)

For this tank, withdrawal losses are significant compared to standing storage losses. This is as one would expect for a fixed roof tank, which cannot compensate when being filled.

2.5.2 Example of an External Floating-roof Tank

The tank in this example is identical in shape and location to the tank in the example given in section 2.4. The contents are crude oil, with a Reid vapour pressure of 5.

The yearly average of the average daily surface temperature works out as 23.2°C (73.72°F), which gives an average vapour pressure of 25.8 kNm^{-2} (3.74psi).

With typical tank fittings (as section 2.4) and light rust covering the tank shell, the yearly results are as follows:

Rim seal losses = 96.9 kg (213.6 lb)

Withdrawal losses = 13.7 kg (30.3 lb)

Deck fitting losses = 364 kg (803.3 lb)

Here the withdrawal losses account for a tiny 2.9% of the total losses. The deck fitting losses dominate the standing storage losses.

If the deck fittings are all fitted with gaskets, and the rim seal mechanism is changed to a liquid mounted primary seal with a rim mounted secondary seal, the standing

storage losses are reduced markedly. If the shell condition is changed to dense rust, the picture is as follows:

Rim seal losses = 19.4 kg (42.86 lb)
Withdrawal losses = 68.8 kg (151.6 lb)
Deck fitting losses = 36.3 kg (79.98 lb)

Now, the withdrawal loss accounts for 55.6% of the total. The standing storage loss is still dominated by the deck fitting losses. Changing the rim sealing mechanism to a vapour mounted seal leads to the situation where the rim seal losses dominate the total losses.

2.5.3 Example of an Internal Floating-roof Tank

It is assumed that the tank is 21.3 m (70ft) diameter, 3790 m³ (one million US gallons) volume, with the roof supported by one column of 0.3 m (1ft) diameter. The tank has 50 turnovers per year. Shell and roof are painted white, with the paint in good condition. The shell is covered in light rust. The rim of the internal floating roof is fitted with a liquid mounted primary seal and a secondary seal. The deck is welded, with the following fittings:

One 25 cm (10-inch) diameter vacuum breaker, weighted, mechanically actuated, gasketed.

One 91 cm (36-inch) diameter ladder well, with gasketed sliding cover.

One 61 cm (24-inch) diameter built-up column well, with gasketed sliding cover.

Twenty-one adjustable roof legs.

One 61 cm (24-inch) sample well, with a 10% open slit fabric seal.

One automatic gauge float well, with gasketed bolted cover.

One 61 cm (24-inch) diameter access hatch, with gasketed bolted cover.

The tank is located in Birmingham, Alabama, which has the following meteorological conditions:

Daily average ambient temperature = 16.7°C (62.2°F)

Annual average maximum temperature = 22.9°C (73.2°F)

Annual average minimum temperature = 10.6°C (51.1°F)

Average wind speed = 3.2 m.s⁻¹ (7.2 mph)

Annual average daily insolation = 15 MJ.m² (1345 BTU/ft²)

Tank contains gasoline, with a Reid vapour pressure of 13, and a vapour molecular weight of 62 kg.kmol⁻¹.

The calculated yearly emissions are:

Rim seal losses	= 543 kg (1197.0 lb)
Withdrawal losses	= 54.3 kg (119.6 lb)
Deck fitting losses	= 1329 kg (2931.5 lb)
Deck seam losses	= 0 kg (0 lb)

Deck fitting losses dominate the total, despite the gasketing. If the more typical, ungasketed fittings are used, the deck fitting losses rise to 1719 kg (3789.7 lb). Withdrawal losses rise to 271 kg (597.8 lb) if dense rust is assumed to cover the shell. If the deck is constructed of continuous bolted 1.5m (5ft) wide sheets, emissions from the deck seams become very significant: 1616 kg (3562.4 lb), comparable to typical losses from the deck fittings.

2.5.4 Summary of Relative Factors Affecting Emissions

For fixed roof tanks, the withdrawal losses form a significant fraction of the total losses. Due to the simplicity of shape and of fittings of fixed roof tanks, however, the equations offer limited flexibility for examining the effects of changing parameters.

For floating-roof tanks, it can be seen that the tank configuration and condition determines whether the rim or the deck is the most significant area of evaporative losses. For both internal and external floating-roof tanks, the condition of the shell determines whether the withdrawal losses are an important fraction of the total.

3 PROCESS EQUIPMENT FUGITIVE EMISSIONS

These calculations were developed to estimate fugitive emissions from refineries and other process plant equipment. Typically, leakage from valves accounts for about 60% of losses from process plant, with pumps and flanges representing about 10% and 5% respectively [15].

There are four approaches described in the US EPA's Protocol for estimating emissions [16]. In order of increasing refinement, they are: Average Emission Factor Approach, Screening Ranges Approach, EPA Correlation Approach, and Unit-Specific Correlation Approach.

A detailed history of the development and application of these loss estimation procedures is given in Woods et al [17].

The first two methods are based on old data, collected from process plants likely to be atypical of those currently in operation. The average emission factor approach assigns values for the losses for various types of equipment. These values are multiplied by the number of each of a particular type of equipment in operation. The screening ranges approach was designed to be operated together with a leak detection and repair (LDAR - not to be confused with LIDAR) programme; the screening procedure is carried out to find any equipment showing a serious leak, and this leak is then subsequently repaired. The screening value for a piece of equipment is the concentration of hydrocarbons recorded by a probe close to the appropriate part of the equipment. The appropriate sites for measurement on an equipment component are outlined in the EPA's protocol [16]. The screening ranges method is not designed to give an accurate measure of the emissions from the plant under

inspection.

The EPA correlation approach requires screening data for a representative sample of equipment components to be collected. These data are then entered into the correlations provided by the US EPA to determine the emissions rates. The value of emissions for this representative sample can then be scaled up to give an estimate of the emissions for the whole plant.

The unit-specific correlation approach requires new correlations to be developed based on a screening and bagging survey. Bagging components, described in the EPA's protocol [16], is a method of determining the true mass emissions from a piece of equipment. The new correlations relate the values from the screening survey to the values obtained from the bagging. This enables the results of a further, extensive screening survey to be converted into mass emissions. This method does not rely on correlations developed previously and therefore no comment as to the accuracy of this method is possible, beyond the general applicability of the screening values as a measure of the emissions from a piece of equipment.

The EPA correlation approach is more sophisticated, and therefore potentially more accurate, than the two simpler methods. Unlike the unit-specific correlation approach, it relies on data presented by the EPA and on the correlations developed by the EPA. For these reasons, the EPA correlations and their development will be concentrated on for the rest of this section.

3.1 DEVELOPMENT OF THE EPA CORRELATIONS

The EPA correlations are based on data collected in the early 1990's by Radian Corporation and Star Environmental [18]. These data were used to generate general petroleum industry correlations. Correlations for the synthetic organic chemical manufacturing industry are based on data collected in the early 1980's [16].

The correlations relate the screening value measured for a piece of equipment to its mass emissions. The screening value is the volumetric concentration of hydrocarbons measured at the point of maximum leakage of the component.

The screening value is some measure of the leaking of the component, but it is not clear in advance how generally applicable a single correlation will be over a range of different component types and sizes. The studies mentioned above used statistical and visual comparisons to group the data by component type and fluid being serviced.

Two special cases of screening values are highlighted (for example [19]). Those components that show no increase over the local background concentrations have been shown in some cases to leak appreciably. These components, called default-zero components, are assigned a single mass emission value. More significantly, those components that show a local concentration greater than the maximum measurable by the organic vapour analyser in use are also assigned a single leak rate. This is clearly an unreasonable assumption, and since these components, known as pegged components, are by definition the greatest leakers under inspection, this simplification is cause for concern. For example, Woods et al [17] reported that the pegged components accounted for 90% of total emissions from a polystyrene plant. In terms of numbers, this was only 3 of the 1566 flanges and 6 of the 205 valves measured.

3.2 UNCERTAINTIES IN THE EPA CORRELATIONS

The sole assumption concerning the development of the correlations for estimating emissions from process equipment is that the concentration of hydrocarbons measured at the point maximum leakage of a component is a measure of the total emission rate from that component. This assumption is suspect, given that the screening values are known to vary over orders of magnitude, even over a single day [19].

For some equipment types, different correlations are presented based on the fluid in the process line. This split accounts for the different leak mechanisms of gas and liquid. There is an arbitrary distinction between light and heavy liquid; this split could depend on the physics of the sealing mechanism.

The measured hydrocarbon concentration at the point of maximum leakage is used as the input for the correlation. If there is more than one leak from a piece of equipment then this is neglected.

Wind flow around the component affects the relationship between the measured concentration and the leak rate. This effect has been investigated, but no work has been published to date. It is not considered in the correlations.

3.3 STATISTICAL METHOD USED

A power-law function was developed for each group of components, relating the screening value to the mass emission rate. The experimental data was plotted on a log-log graph and a linear regression was done. In transforming back to a linear scale, a "scale bias correction factor" was used. This factor is intended to correct bias in the regression, due to it being done on a log scale. However, the conditions for a linear regression to be applicable do not seem to be violated, and the estimates are better if the scale bias correction factor is not applied: the sum of squares of the residuals for the valve data is lower if scale bias correction is not used.

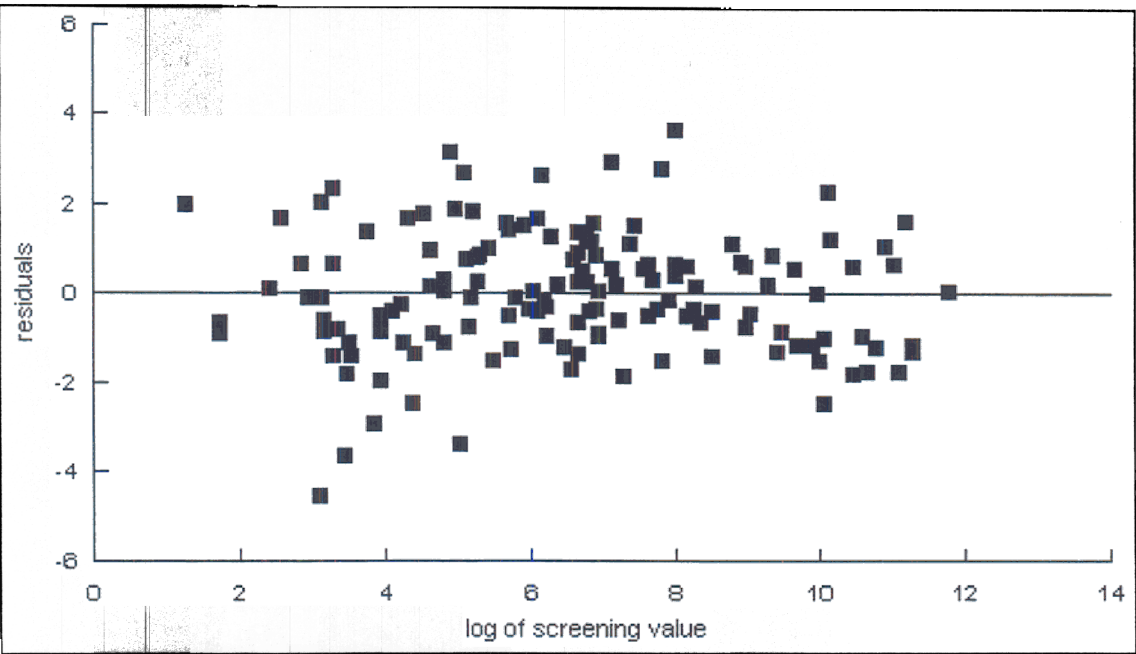


Figure 4 - Residual Plot for Valves

Figure 4 shows a plot of the residuals (i.e. the difference between the calculated values and experimental values of the logarithm of mass emissions) against the log of the screening value for valves, the largest set of data. As can be seen, there is no evident bias in the size of the residuals. This implies strongly that no scale bias correction factor is necessary.

4 OVERALL CONCLUSIONS

4.1 STORAGE TANKS

The API tankage calculations were designed to give a value of the average yearly emissions from a given tank. Given the variety of liquids stored, the combinations of fittings and sealing methods and the simplifications in the correlations, it is perhaps surprising that the correlations show such good agreement with short-term measured values [5, 20]. There is, however, a limit to the accuracy obtainable by invoking general correlations for the various tank fittings and seal types. The conclusions below include some of the findings of the Swedish workshop led by Stripple and Galle [21].

The large change in estimated emissions, reported by Concauwe [20], caused by the addendum to the external floating-roof calculations [13] indicates that most of the evaporative losses are coming from a few sources, and that inaccuracies in these correlations leads to inaccuracies in the total estimate.

The simplifications used to generate the insolation parameters, which lead to the average liquid temperatures and the liquid surface temperatures are crude; setting up a rigorous computer method for analysing the local parameters should be feasible and since insolation is not likely to vary greatly over small areas, should be possible using data from existing weather stations.

There are two significant problems with the analysis of wind effects on the emissions:

- i) The wind speed at the tank site is unlikely to represent the wind speed over the fittings and rim seals themselves.
- ii) The use of an annual average wind speed will not account correctly for nonlinear wind effects.

The second problem is surmountable by using daily data from a weather station and calculating the emissions day-by-day; given current computing power, this option should be feasible to implement. However, initial calculations seem to suggest that this does not have a significant impact on the estimate. The problem of where the wind speed is measured has been addressed by the API [14], but they did not come to any definitive conclusions. Coupling data on tank levels (if recorded) with experimental data relating the wind speed at various tank heights to the locally measured wind speed could improve accuracy. The problem of gusty wind cannot be tackled in this way, but any brief gust of wind is unlikely to have significant additional impact on the emissions.

Although effort has been made to ensure the data needed as inputs to the correlations are simple to obtain, certain data such as the condition of the tank seals is not likely to be available while the tanks are in operation. The tank contents may also not be

routinely sampled, so the properties used in the equations could be wrong [5]. If the contents of the tanks are known, the vapour pressure at various conditions can be calculated to reasonable accuracy using Raoult's law [3].

The vapour pressure function, which is used to relate the vapour pressure of the tank contents to the emission rate, is an area that requires further study, both theoretically and experimentally. The crude oil factor is another area that needs exploration. Possibly a new function or correlation could be developed to supersede both the vapour pressure function and the crude oil factor.

A survey of tank manufacturers to determine the variety and morphology of the various rim seals and deck fittings in current service could indicate the way forward in improving the accuracy of the published calculations: if, for example, there are only a few standard designs for specific deck fittings, it would limit the amount of work to develop theory and design experiments for estimating the levels of emissions from each. It would then be possible to consult the original plans for the tanks to determine the leak sources exactly. The problem of aged tanks with poor seals and fittings could be addressed by making companies aware of their responsibilities under BATNEEC and in terms of a cost-benefit analysis to show how much valuable product they are losing.

4.2 PROCESS EQUIPMENT

The calculations for estimating losses from process plants have grown out of screening surveys designed to allow leak detection and repair programmes to be carried out. Unlike evaporative losses from tanks, which can be assumed to happen in a regular and predictable way, losses from process lines are by nature caused by faulty seals and connections.

The data collected to generate the petroleum industry correlations were gathered in California; they were shown to be significantly different to those collected in the late 1970's. These data may not represent current UK refineries and process plants.

Sampling to generate the correlations was carried out on a non-random, convenience sampling basis: those components that were easiest to reach were sampled. This could lead to a bias in the correlations, since the data may be unrepresentative.

Multivariate analysis was carried out to group the components sampled, by type and by fluid in service. However, the amount of data for each component was limited, and in almost all cases was below the 30 data pairs recommended by the EPA's Protocol. The final grouping of components was largely pragmatic, to ensure that each group contained enough data.

It is vital that the sample used in the screening survey is representative of the whole plant. For example, although a single generic equation is provided for estimating emissions from valves, clearly some valve types leak more than others, and some valves are leakless. Using an unrepresentative sample as the basis of the emissions estimate will lead to an erroneous estimate.

The losses are unpredictable, but given a large enough sample, statistical methods should be applicable. The limited quantity of data collected, the methods used to analyse it, and the representativeness of the data are all causes for concern.

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