

NPRI Guidance on estimating atmospheric emissions from storage tanks



EXECUTIVE SUMMARY

This document presents guidance for estimating atmospheric emissions from storage tanks. The guidance address both the evaluation of emissions from storage tanks receiving stabilized or weathered product, as well as those receiving flashing products. A tiered approach is used to accommodate the range of input information available, and the relative importance of the assessed emissions contributions.

A standard tool used for many years by practitioners to estimate emissions from tanks receiving stabilized or weathered products is the US Environmental Protection Agency's (EPA's) TANKS model. Historically, TANKS has implemented the calculation procedures presented in AP-42, Chapter 7: Liquid Storage Tanks. In March of 2020, an update to AP-42, Chapter 7 was issued to specifically address known errors and deficiencies in TANKS Version 4.09d; however, the TANKS model was not updated. US EPA announced that while it is still making this tool available, it is no longer supporting it.

This document summarizes the key technical changes made to AP-42, Chapter 7 and it is expected that users will create their own spreadsheet or other software tools to apply the most current version of AP-42, Chapter 7, or access commercial solutions that may become available.

Neither AP-42, Chapter 7 or TANKS 4.09d provide guidance for assessing flashing emissions. Hence, specific guidance on this matter is also provided.

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LIST OF ACRONYMS

AP-42	-	The document codifying the air pollutant emission factors for stationary sources, available from the US EPA's Emission Inventory Branch in the Office of Air Quality Planning and Standards (https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emissions-factors).
API	-	American Petroleum Institute
BS&W	-	Basic Sediment & Water
CDPHE	-	Colorado Department of Public Health & Environment
ECCC	-	Environment and Climate Change Canada
HAP	-	Hazardous Air Pollutant
LACT	-	Lease Automatic Custody Transfer
NPRI	-	National Pollutant Release Inventory
RVP	-	Reid Vapour Pressure
TCEQ	-	Texas Commission on Environmental Quality
TVP	-	True Vapour Pressure
US EPA	-	United States Environmental Protection Agency
VOC	-	Volatile Organic Compounds

Introduction

This document presents guidance for estimating atmospheric emissions from petroleum storage tanks for the purpose of reporting to ECCC's NPRI. Two types of emissions are considered: routine evaporation losses from tanks containing weathered or stabilized petroleum liquids (see Section [Estimation of emissions from tanks containing weathered or stabilized petroleum liquids](#)), and flashing losses (see Section [Estimation of flashing losses from production storage tanks](#)).

The overall aim is to direct users to established procedures for estimating emissions from storage tanks, provide helpful tips on where to find necessary input information and how to bridge data gaps, and to delineate simplifying assumptions or methods that may be applied based on a user's specific circumstances.

US EPA published in March 2020 an update of AP-42 Chapter 7: *Liquid Storage Tanks* that contains more than 200 pages presenting emissions estimating methodologies for storage tanks of various types and operating conditions. This new update also clearly states that TANKS 4.09d contains known errors and is no longer supported. While TANKS 4.09d is no longer supported, copies are still available on the US EPA's web site at <https://www.epa.gov/air-emissions-factors-and-quantification/tanks-emissions-estimation-software-version-409d>. The reason TANKS 4.09d is no longer supported is stated as follows:

The TANKS model was developed using software that is now outdated. Because of this, the model is not reliably functional on computers using certain operating systems such as Windows Vista or Windows 7. We are anticipating that additional problems will arise as PCs switch to the other operating systems. Therefore, we can no longer provide assistance to users of TANKS 4.09d. The model will remain on the website to be used at your discretion and at your own risk. We will continue to recommend the use of the equations/algorithms specified in AP-42 Chapter 7 for estimating VOC emissions from storage tanks. The equations specified in AP-42 Chapter 7 (<https://www.epa.gov/ttn/chief/ap42/ch07/index.html>) can be employed with many current spreadsheet/software programs.

The NPRI guidance provided herein summarizes the essentials of storage tanks emissions estimation methodologies based on the updated US EPA AP-42, Chapter 7 (March 2020). This NPRI guidance is intended to be more straightforward and shorter than the voluminous AP-42, Chapter 7, and reflects the current understanding on how aboveground liquid storage tanks work, how they generate emissions, how they are monitored or tested, and what data are typically most readily available for emissions determination.

The AP-42 Chapter 7 methodologies for estimating atmospheric emissions (i.e., standing and working losses) from fixed-roof and floating-roof tanks apply to tanks containing weathered or stabilized petroleum liquids. The presented methods consider routine operations and selected non-routine events and circumstances (i.e., landing of floating roofs, tank cleaning and degassing, use of variable vapour space

tanks, averaging times down to one month, internal floating roof tanks with closed vent systems, case-specific circumstances for estimating liquid surface temperatures, and heating cycles in fixed-roof tanks). Section [Estimation of emissions from tanks containing weathered or stabilized petroleum liquids](#) herein presents simplified guidance for application of the AP-42, Chapter 7 methods. Emissions from fugitive equipment leaks on tanks designed as closed systems (i.e., tanks featuring a vapour collection and control system), are considered to be part of facility-wide emissions fugitive equipment leaks (to be reported to NPRI as “fugitive releases to air”), and not storage losses.

Whenever a hydrocarbon liquid exists in contact with a gas at pressurized conditions, it will tend to absorb some of the gas. Subsequently placing that liquid in an atmospheric storage tank results in the dissolved gas being released as flashing losses, which is a rapid form of evaporation (e.g., a boiling event). Flashing losses typically occur at oil and liquids-rich natural gas production facilities, and potentially at some downstream oil and gas facilities. Section [Estimation of flashing losses from production storage tanks](#) delineates methods for estimating flashing losses.

Releases to air from the storage of liquids in tanks, releases to air associated with liquid storage tank operations, releases to air from the transfer, loading and unloading of liquids to and from storage tanks, losses to air associated with the storage of liquids in tanks, and losses to air associated with the cleaning, degassing and maintenance of storage tanks must be reported under On-site Releases/Releases to air/Storage tank and related handling releases category. Find complete information about the NPRI reporting requirements for all substances and sectors in the [Canada Gazette Notice](#) and the [Guide for reporting to the NPRI](#).

Estimation of emissions from tanks containing weathered or stabilized petroleum liquids

Recommended approach (AP-42)

The recommended approach for estimating atmospheric emissions from storage tanks containing weathered or stabilized products is to apply the methods detailed in AP-42, Chapter 7.

ECCC does not recommend the use of TANKS 4.0d. Users should either implement the latest AP-42 Chapter 7 procedures as a spreadsheet or other suitable software tool, or access commercially available solutions that feature the latest procedures. The level of effort required to implement your own software solution will depend on your specific circumstances (i.e., some of the special cases may not apply to your circumstances).

Key changes in the newest release

AP-42, Chapter 7 presents detailed guidance for estimating and speciating atmospheric emissions from storage tanks containing weathered or stabilized products.

The key methodological changes made to AP-42, Chapter 7 that address known errors or deficiencies in TANKS 4.09d are delineated below:

1. **Temperature effects** – the calculation procedures previously used simplified techniques for estimating temperature effects, and these methods were subject to significant uncertainty (partly due to the simplifications and assumptions that have been applied, and partly because of the use of average metrology). Their use was an unnecessary carry-over from when computer access was not widely available. The updated procedures now utilize more refined and reliable methods, and allow for the use of measured bulk liquid temperatures where such information is available.
2. **Fully insulated tanks** – such tanks were previously assumed to have no breathing losses and no provisions were made to account for breathing-induced losses from any temperature cycling caused by tank heaters. The new procedures now allow for heater-induced breathing losses.
3. **Partially insulated tanks** – the calculation procedures have been updated to handle these cases, which are reasonably common in practice. A partially insulated tank is one that has insulation on the shell but not on the roof. Treating this type of tank as if it were fully insulated would understate the amount of emissions since significant heat transfer may occur through the tank roof.
4. **Floating roof landing losses** – procedures have been developed for estimating these previously unaccounted for emissions contributions. Normal practice is to minimize the potential for such events. Nonetheless, where they do occur (e.g. when tanks are taken out of service or in order to reduce RVP for summer), they can be a significant source of emissions.

5. **Tank cleaning losses** – procedures have been developed for estimating these emission contributions. Larger tanks may only be cleaned once every 10 years. Smaller tanks may get cleaned much more regularly; especially production tanks that experience sand or sludge accumulation. The current methodology is specifically for estimation of emissions while forced ventilation is operating in the tank, regardless of whether or not cleaning operations are taking place.
6. **Working losses** – the procedures for estimating working losses previously relied on the differences in inflow and outflow rates to determine working losses. This approach is much less reliable than using actual data on liquid-level changes to determine the actual amount of vapour physical displacement.
7. **Leaking pressure vacuum valves** – the model does not account for leakage from pressure vacuum valves and thief hatches on the tank. Leakage past such vents should be estimated and reported to the NPRI (see section 7 under [Important Considerations](#).)
8. **Special cases** – the updated procedures now handle cases involving internal floating-roof tanks with closed vent systems. This refers to internal floating-roof tanks that vent to the atmosphere, but which have self-closing vents rather than the more typical open vents. US EPA references an API document, with a recommendation of simply applying a 5% reduction from the estimated emissions for a freely vented internal floating-roof tank.
9. **Other matters** – use of default speciation profiles is discouraged. Preference is given to using actual case-specific vapour analysis results or predicting vapour compositions based on known case-specific liquid compositions. A potential issue with the latter approach is that it will not necessarily detect all compounds of interest. For example, some lighter compounds will exist in the liquid in concentrations too low to be detected, but many still occur in material concentrations in the vapour space (e.g., H₂S and other reduced sulphur compounds).

Basic information requirements

The basic information needed to estimate storage losses from tanks containing such liquids is as follows:

1. **Tank data** – this includes, for each tank, the type of tank (i.e., fixed-roof or floating roof), its physical dimensions, working volume, paint colour and condition, details on the surfaces insulated (i.e., shell, roof or both), types and number of fittings used on floating-roofs (defaults are available in Tables 7.1-12 to 7.1-15 of AP-42, Chapter 7 if actual values are unknown), set-points of any pressure-vacuum (or breather) valves used on the tanks, identification code or name of the stored product, and details of any systems used to heat the tank. The tank data is usually available from the tank datasheets in the facility's equipment manuals, and from the tank design drawings.
2. **Characteristics of the petroleum liquid** – the minimum information needed on the liquid product is its API gravity (or density), molecular weight and RVP or detailed chemical analysis. The RVP may vary with time of the year and, in such cases, will generally tend to be greater in the winter than in the summer. Lesser variations may occur for the other parameters. Potential sources of a products properties include its safety data sheet, Crude Monitor (an online database of crude oils available at <https://www.crudemonitor.ca/>), and the crude characteristics booklet

published by Enbridge Pipelines Inc. at https://www.enbridge.com/~media/Enb/Documents/Shippers/Crude_Characteristics_Booklet.pdf?la=en.

3. **Vapour composition** – The basic procedures for estimating storage losses determine the total amount of petroleum vapour emitted and require an estimate of the vapour molecular weight, but do not provide detailed speciation of these emissions as is necessary for NPRI reporting purposes. To determine the emissions of specific NPRI reportable substances, it is necessary to speciate the assessed emissions. This may be done by applying a vapour analysis to the assessed emissions using the procedures presented in Section [Emission speciation](#).
4. **Activity levels** – the key activity parameter that must be determined is the cumulative amount of incremental liquid-level increases in the tank during a period of interest (i.e., per month or annum). Incremental liquid-level increases (i.e., positive incremental liquid level changes) physically displaces vapours from the tank. The resulting atmospheric emissions are termed working losses (see Equation 1-35 in AP-42, Chapter 7). The sum of all incremental liquid-level increases is often expressed in terms of the number of tank working-volume turnovers per year (also simply referred to as turnovers per year), N , which may be expressed by the following relation:

$$N = \frac{V_Q}{V_W}$$

Equation 1

Where,

V_Q Net working loss throughput (as defined by for Equation 1-35 of AP-42, Chapter 7), which is also the cumulative annual volume of positive physical displacement due to the sum of all incremental liquid-level increases (m^3).

V_W Working volume of the storage tank (m^3).

$$V_W = (H_{LX} - H_{LN}) \cdot \pi \frac{D^2}{4}$$

Equation 2

Where,

H_{LX} Maximum liquid height (m). If this value is unknown, AP-42, Chapter 7 recommends using a value of 0.3048 m less than the shell height for vertical tanks, and for horizontal tanks, to use $\left(\frac{\pi}{4}\right) \cdot D$ where D is the inside diameter (m) of a vertical cross-section of the horizontal tank.

- H_{LN} Minimum liquid height (m), If this value is unknown, AP-42, Chapter 7 recommends using a value of 0.3048 m for vertical tanks and 0 m for horizontal tanks.
- D Inside tank diameter (m).

Table 1 below presents procedures for estimating the net working loss throughput experienced by a tank as a function of its operating mode and activity levels.

Table 1: Methods for estimating the total annual volume of positive displacement for use in calculating working losses.		
Type of Inflow	Type of Outflow	Determination of Total Annual Volume of Positive Displacement
Batch	Batch	<p>Equals the annual receipt volume if there is no overlap of inflow and outflow batch events.</p> $V_Q = V_{AR}$ <p>Equation 3</p> <p>Where,</p> <p>V_{AR} = Annual volume of liquid hydrocarbon received by the storage tank (m³).</p> <p>If there is the potential for some overlap of inflow and outflow batch events, then V_Q will be less than V_{AR}, but Equation 3 may still be used to obtain a conservative estimate of V_Q.</p>
Continuous	Batch	<p>If the inflow rate is relatively constant but the outflow occurs in batch events, then V_Q may be estimated using the following equation:</p> $V_Q = V_{AR} \cdot \left(1 - \frac{Q_{IF}}{Q_{OF}}\right)$ <p>Equation 4</p> <p>Where,</p> <p>Q_{IF} = average liquid hydrocarbon inflow rate (m³/h)</p> <p>Q_{OF} = average liquid hydrocarbon outflow rate during batch events (m³/h).</p>

Table 1: Methods for estimating the total annual volume of positive displacement for use in calculating working losses.		
Type of Inflow	Type of Outflow	Determination of Total Annual Volume of Positive Displacement
Batch	Continuous	<p>If the inflow occurs as a series of batch events and the outflow occurs continuously at a relatively constant flowrate, then V_Q may be estimated using the following equation:</p> $V_Q = V_{AR} \cdot \left(1 - \frac{Q_{OF}}{Q_{IF}}\right)$ <p style="text-align: center;">Equation 5</p> <p>Where,</p> <p>Q_{IF} = average liquid hydrocarbon inflow rate during batch events (m³/h)</p> <p>Q_{OF} = average liquid hydrocarbon outflow rate (m³/h).</p>
Continuous or Semi-continuous	Continuous or Semi-continuous	<p>In these cases, the value of V_Q may be assessed using the following equation for vertical cylindrical tanks:</p> $V_Q = \frac{\pi D^2}{4} \sum \Delta h_+$ <p style="text-align: center;">Equation 6</p> <p>Where,</p> <p>D = Inside tank diameter (m).</p> <p>Δh_+ = Incremental increases in the liquid level in the tank between successive liquid-level readings during the year of interest (m). Zero and negative changes are ignored.</p> <p>Otherwise, the value of V_Q should be assessed using the following general equation:</p> $V_Q = \sum \Delta V_+$

Table 1: Methods for estimating the total annual volume of positive displacement for use in calculating working losses.		
Type of Inflow	Type of Outflow	Determination of Total Annual Volume of Positive Displacement
		<p style="text-align: center;">Equation 7</p> <p>Where,</p> $\Delta V_+ =$ <p style="text-align: right;">Incremental increases in the product inventory in the tank between successive inventory readings (m³). Zero and negative changes are ignored.</p>

5. **Tank void space** – for fixed-roof storage tanks, the typical liquid level in the tank is needed for use in determining breathing losses. Most tanks and tank farms are designed with a certain amount of surplus capacity as a contingency for potential disruptions to the product supply and sales systems. In other cases, the tanks may be used for merchant storage applications and remain filled during periods of low demand and be drawn down during high market demand. Hence, the actual amount of void space and its variability with time should be carefully examined. Some general rules of thumb are as follows:
 - Tanks in continuous flow-through service will typically be maintained at a liquid level equal to 50% of the tank’s working capacity.
 - At production facilities, tank levels are often maintained at 50% or less of their working capacity.
6. **Site-specific meteorological conditions** – this includes daily average ambient temperature, hourly average maximum temperature, hourly average minimum temperature, average wind speed, average solar insolation factor, and atmospheric pressure. Some of these parameters will vary materially by season and month of the year.

Emission speciation

The preferred option for speciating emissions of product vapours from storage tanks is to use site-specific vapour analyses applicable to the assessed emissions contributions. Care should be taken in using default vapour analyses based simply on the type of product, as there may be significant compositional variations within a given product category. This is especially true for trace or secondary constituents of a product.

The composition of the vapour emitted from a petroleum liquid will differ from the composition of the petroleum liquid and will vary with the product temperature. Both phases will comprise the same mix of components; however, the vapour phase will contain greater concentrations of the more volatile

components and lower concentrations of the less volatile components. Moreover, some components of interest may be readily detected in the vapour phase and either be undetected in the liquid phase (i.e., exist in the liquid phase in concentrations below the lower detection limits of the applied analytical method) or be excluded as a target analyte for a routine liquid analysis.

Section 7.1.4 of AP-42, Chapter 7 delineates procedures for estimating the vapour composition based on a known liquid analysis. The use of Raoult's Law is recommended for hydrocarbon mixtures. Henry's law is recommended for application to dilute aqueous solutions such as wastewater.

If no vapour-phase data are available, the preferred method for determining emissions for H₂S released during storage is to perform site-specific sampling and analysis of the tank vapour space.

Determination of local meteorological parameters

In calculating the tank emissions for a given facility, observed average temperatures from either the historical weather dataset or the "Canadian Climate Normals" dataset for the nearest and representative meteorological data can be used. This data can be obtained online via the ECCC historical data portal at [Historical Climate Data - Climate - Environment and Climate Change Canada \(weather.gc.ca\)](http://weather.gc.ca).

The following links provide solar data for Canada:

1. [Solar resource data available for Canada \(NRCan\)](#).
2. [NASA Prediction of Worldwide Energy Resources](#).

Important considerations

1. Produced water tanks

Produced water tanks having an oil layer on top should be modelled as oil storage tanks. Two sets of calculations should be performed: one to estimate any flashing losses due to the amount of hydrocarbon liquid carry-over to the tanks (if applicable), and one to predict routine working and breathing losses from the tank as if it contains crude oil consistent with the hydrocarbon liquid carry-over. The latter emission contributions should be assessed in accordance with the most current version of AP-42, Chapter 7.

2. Gas blanketed tanks

Gas blanketed tanks that vent to atmosphere, tanks that are vapour balanced and tanks that experience flashing losses should be modeled using a working loss turnover (saturation) factor, K_N , of 1 (see Equation 1-35 in AP-42, Chapter 7).

3. Tank working volume

If the maximum liquid height is unknown, for vertical tanks use 0.3048 m less than the shell height and for horizontal tanks use the inside diameter of the tank. If the minimum liquid height is unknown, for vertical tanks use 0.3048 m and for horizontal tanks use 0 m.

4. Floating roof landings

When a floating roof lands at its minimum allowable vertical position in the tank, vacuum breaker vents automatically open and these remain open until the roof is re-floated. While the vacuum breakers are open and there is still liquid in the tank, the tank will behave as a fixed roof storage tank resulting in increased emissions. For this reason, operators tend to avoid landing a floating roof wherever possible. If such roof landings occur in a particular year, then these need to be assessed separately and added to the assessed working and breathing emission contributions for when the floating roof is not landed.. These contributions need to be assessed separately using the procedures presented in Section 7.1.3.2 of AP-42, Chapter 7.

5. Tank cleaning

The emissions from tank cleaning are attributed to the ventilation emissions for each day of forced ventilation while volatile material remains in the tank. Where such emissions are applicable, they should be assessed separately using the procedures presented in Section 7.1.3.4 of AP-42, Chapter 7.

For floating roof tanks, any emissions associated with landing the roof before the start of tank degassing, and during refloating of the roof when the tank is being put back into service, need to be assessed separately (see Section 7.1.3.2 of AP-42, Chapter 7), and added to the assessed tank cleaning emissions.

At production sites, tanks may be routinely cleaned to remove accumulated sand and sludge. However, downstream of production sites the accumulation of solids and sludge is managed by applying strict BS&W standards and potentially by using mixers to help keep any solids in suspension. Hence, the frequency of tank cleaning events downstream of production sites tends to be quite low. Many tanks are only cleaned once every 10 years to allow for API 653 inspections, and sooner if issues requiring tank cleaning arise. When a tank is cleaned, it is first drained of liquids, isolated, degassed and then any sludge or solids are physically removed (e.g., by using pressurized water jets to break up the material and vacuum trucks to remove it). Sometimes a light solvent and chemicals may be introduced into the tank to help dissolve and manage emissions from the sludge.

Forced ventilation of the tank is maintained during the degassing phase and onwards as needed to keep vapour concentrations safely below the lower flammable limit, and, where workers are to enter the tank without supplied breathing air, within applicable occupational guidelines.

6. Flashing losses

AP-42, Chapter 7 does not provide any procedures for assessing emissions from tanks due to flashing losses. Such procedures are described in Section [Estimation of flashing losses from production storage tanks](#).

7. Pressure Tanks

Tanks that are operated at pressures between 17.2 and 103.4 kPag (or 2.5 and 15 psig) are low-pressure tanks and are potential sources of storage losses where the tanks feature a pressure relief valve but is not connected to a vapour collection and control system. The extent of emissions in these cases is a function of the set pressure of the pressure relief device. The standing and working losses can be assessed using the procedures described in Section 7.1.3.1 of AP-42, Chapter 7.

Fugitive losses from high-pressure tanks are estimated as fugitive equipment leaks and are not addressed by AP-42, Chapter 7. These losses should be considered for the NPRI reporting, but they are outside the scope of this document.

Estimation of flashing losses from production storage tanks

The emissions from a tank that experiences flashing losses, will generally be dominated by these losses, but will also potentially experience working and standing losses in addition to flashing events. The routine standing and working losses as described in Section [Recommended approach \(AP-42\)](#) must also be estimated and added to the estimated flashing losses.

Figure 1 presents a simplified flow diagram of a basic flash-gas scenario. A legend of the streams in Figure 1 is presented in Table 2. The activity data for the storage tanks should include the true oil or condensate production rate and any recycled volumes. If vapours are routed to a control device, the control efficiency of the device should be applied to the flashing losses as well as to the standing and working losses. If vapours are routed to a compressor for injection into a gas line or process, the control efficiency may be assumed to be 100% whenever the compressor is on-line.

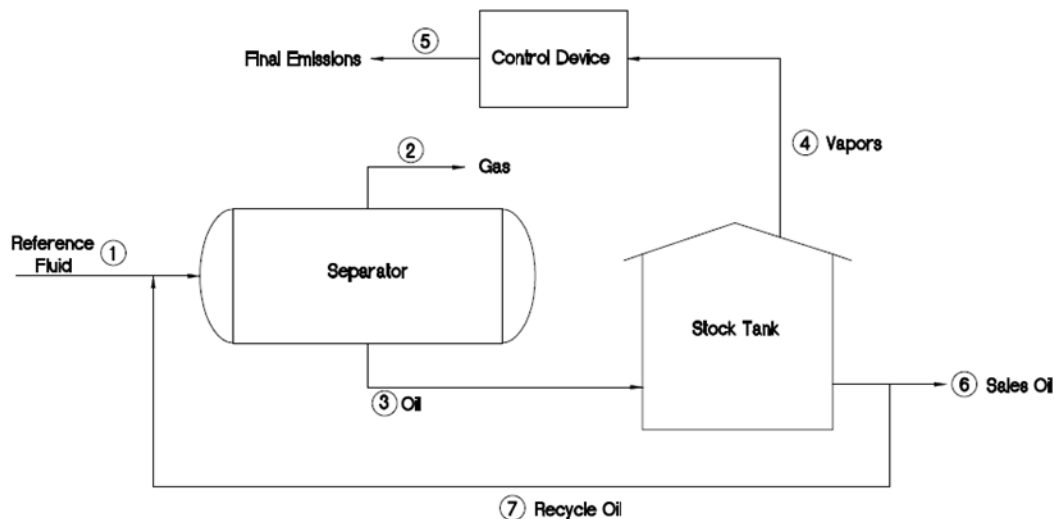


Figure 1: Simplified flowsheet diagram of a basic flash gas scenario.

Stream No.	Stream Name	Description/Comment
1	Reference Fluid	The reference fluid defines the overall composition of the multi-phase production stream entering the production facility being considered. Typically, the inlet stream comprises a mixture of oil or condensate, associated natural gas and water.
2	Gas	This is the associated gas separated from the inlet stream (Stream 1).

3	Oil	This is the hydrocarbon liquid phase separated from the inlet stream (Stream 1). It contains a certain amount of dissolved natural gas, which flashes out when the oil experiences the downstream low-pressure conditions of the atmospheric storage tank.
4	Vapours	This is the flash gas released from the oil received from the separator.
5	Final Emissions	The amount and composition of the final emissions is a function of the type of vapour control device installed (if any).
6	Sales Oil	This is weathered oil (i.e., it contains little, if any, dissolved natural gas).
7	Recycle Oil	This is off-specification product return by the LACT unit or automatically drawn from the bottom of the storage tanks for reprocessing. Recycling may occur where the pressure vessel located upstream of the storage tanks is a heated separator or a heater-treater. Not all production facilities feature oil recycling.

The amount of emissions may be measured directly using flow metres and speciated based on analyses of the vented gas. However, this is costly to do. Common practice is to estimate the amount of emissions. The uncontrolled emissions contribution due to product flashing, L_F , may be estimated using the following relation:

$$L_F = k_F \cdot V_O \cdot (1 + k_R)$$

Equation 8

Where,

k_F Average flash-gas factor (m^3 of flash gas per m^3 of oil produced).

k_R Average oil recycle factor (dimensionless value between 0 and 1).

The default value is 0, which means no recycling is occurring. If recycling is occurring then a typical value is 0.15; however, user-specified values may be entered.

V_O Volume of oil produced (m^3)

If monthly input data are available, then the following relation may be applied:

$$L_F = \sum_{j=1}^{j=12} L_{Fj} = \sum_{j=1}^{j=12} k_{Fj} \cdot V_{Oj} \cdot (1 + k_R)$$

Equation 9

Where,

k_{Fj} Average flash-gas factor (m^3 of flash gas per m^3 of oil produced) for month “j”.

V_{Oj} Volume of oil produced (m^3) during month “j”.

The following sections describe methods for determining the flash-gas factor.

Measurement techniques

In this case, a pressurized sample of the liquid being dispensed to the storage tank is obtained at the desired separator operating conditions and is then subjected to a physical flash-liberation test by a qualified laboratory. The results of that test are the measured flash-gas factor and flash gas analysis (or speciation profile).

A methodology for performing flash liberation tests is presented by CDPHE (2017) in PS Memo 17-01. The pressurized liquid hydrocarbon sample is conditioned in the laboratory and depressurized in a controlled environment representative of field conditions (temperature and pressure). During depressurization, the volume of gas liberated from the initially pressurized liquid hydrocarbon (i.e. “preflash” crude oil or condensate), and recovered depressurized liquid hydrocarbon (i.e. “storage tank” crude oil or condensate), are directly measured to determine a GOR at field conditions of temperature and pressure. The liberated gas is collected and analyzed to determine the molecular composition of the flash gas. With the data derived from this method, oil and gas companies may directly calculate the mass of flash emissions from a hydrocarbon liquid storage tank without the use of additional process simulation software (e.g. E&P Tanks, commercial process simulators, etc) unless otherwise required.

Use of Process Simulators and E&P TANKS Software

Information Requirements

For the general case, the following basic information is needed:

1. **Oil Analysis** – Either a detailed analysis of the pressurized oil at the separator operating conditions is needed (preferred), or of the sales oil analysis. A C₁ to C₁₀₊ or extended oil analysis is required.
2. **Separator Off-gas Analysis:** A C₁ to C₁₀₊ or extended gas analysis is recommended.
3. **Separator Operating Conditions:** The separator temperature, pressure and approximate GOR when the above oil and gas samples were collected are needed.
4. **Sales Oil Properties:** Both the sales oil API gravity and RVP are needed.

Where a sample of the pressurized liquid hydrocarbon or the associated gas from a separator or treater is collected for laboratory analysis, the results should be subjected to a quality check. For a pressurized liquid hydrocarbon analysis, this should consist of determining the difference between the separator operating pressure recorded at the time the sample was collected, and the calculated bubble-point pressure of the liquid at the recorded separator temperature (the sample is collected upstream of the dump valve during a period when the dump valve is closed). The bubble-point pressure is calculated based on the liquid composition and the separator temperature values using the bubble-point routine. Most commercial process simulators offer the features needed to perform these calculations. The acceptance criteria are presented in Table 3 below as a function of the sampling pressure:

Table 3: Acceptance criteria for sample integrity checks performed based on the difference between the separator operator pressure and the calculated bubble-point pressure of the separator liquid hydrocarbon analysis results.	
Acceptable Range	Field Sample Pressure
±5%	≥ 500 psig
±7%	250 - 499 psig
±10%	100 - 249 psig
±15%	50 - 99 psig
±20%	20 - 49 psig
±30%	< 20 psig

Source: CDPHE (2017)

The quality of a gas or vapour sample is assessed based on the percentage difference between the recorded sampling pressure and the calculated dew-point pressure of the gas. The dew-point pressure is determined based on gas composition and the sampling temperature. An acceptance criterion of within $\pm 30\%$ is recommended.

If the results for a sample fail the quality check, this is a potential indication of one or more of the flowing factors: poor sampling procedures, excessive errors in the recorded sampling pressure and temperature, loss of sample integrity during handling and transport, or poor laboratory procedures. If the source of the deviation cannot be determined and addressed, either a new sample should be collected and analyzed, or the inlet reference fluid to the separator should be assessed using the procedures described in Section [Available options](#) below (Method 2).

Limitations

Estimates of the flashing losses determined using a process simulator are only as good as the quality of the input information used in the simulations, applied modeling assumptions, reliability of the simulation model and suitability of the selected equation of state.

API developed a software tool called E&P Tanks for estimating flashing losses from storage tanks. Although the program continues to be used, API discontinued the sale of E&P Tanks on December 31, 2018 and discontinued supporting issues with installing the software after March 31, 2019. API continues to offer support for existing customers who encounter errors inputting data into software in accordance with E&P Tanks user guide (Publication 4697).

Additionally, various process simulator packages are commercially available. These are typically available for an annual licensing fee and can be relatively expensive.

Available options

Depending on the information available, two different simulation options may be considered for estimating the flash-gas factor and compositions. These methods are, in the order of increasing computational requirements and potentially decreasing accuracy:

- Method 1 - Pressurized-Liquid Flash Simulation:** In this case, a pressurized hydrocarbon liquid sample is collected at the separator operating conditions and analyzed by a laboratory to determine its composition. A flash calculation is performed using a suitable flash program (i.e., E&P Tanks or process simulator). The operating temperature and pressure of the separator are taken from the lab report. Two options may be considered for defining the flash calculation endpoint: (1) the flash endpoint is the temperature of the product in the storage tank and local barometric pressure, or (2) the flash endpoint is the RVP¹ of the storage tank sales oil and a temperature of 37.8°C (100°F):
 - Option 1 does not take into account all of the weathering that occurs when the produced hydrocarbon liquid enters the tank, as the product's TVP will typically weather down to a value less than local atmospheric pressure.
 - Option 2 is equivalent to performing a mass balance based on flow and composition of hydrocarbon liquid entering the storage tank and the flow and composition of the weathered sales product leaving the storage tank. The RVP of the sales oil will vary by month with the values in the winter being greater than those in the summer. Hence, summertime RVP values will result in the greatest peak instantaneous vapour flowrates under Option 2.
- Method 2 - Reference-Fluid Flash Simulation:** This approach is applied where the composition of the pressurized liquid dispensed to the storage tank is unknown for a desired separator operating temperature and pressure, but sufficient input information is available to back-calculate the composition of the fluid entering the separator. First a simulation is performed to predict the composition of the pressurized hydrocarbon liquid leaving the upstream separator. Next, Method 1 is applied to determine the flash-gas factor and composition based on the predicted pressurized hydrocarbon liquid composition.

In performing these calculations, the pressurized liquid analysis should include at least C₁ through C₉ and C₁₀₊, HAPs, He, H₂, N₂, and CO₂. H₂S concentrations and total sulphur content should be determined separately for each phase or sample. If O₂ is present in the analysis results, then this likely indicates some air ingress during the sampling and analysis activities, and the results should then be expressed on an air-free basis.

¹ Reid Vapor Pressure (RVP) is the vapour pressure measured at 37.8°C (100°F) and a vapour-to-liquid ratio of 4:1.

If the RVP of the sales oil is used as the flash endpoint condition, then this is analogous to performing a true mass balance based on the composition and flowrate of the pressurized liquid being dispensed to the tank farm and the composition and flowrate of the weathered sales product leaving the tank. The endpoint flash calculation is performed at a pressure equal to the sales product RVP and at a temperature of 100°F (37.8°C), which is the temperature at which the RVP is determined in accordance with ASTM Method D-323. The RVP of the sales product normally varies on a month-to-month basis due to seasonal effects, and will tend to be greater in the winter than in the summer due to reduced weathering during cold weather. An assessment of annual evaporation losses should evaluate the emissions based on the sum of the monthly contributions.

If the tank operating conditions are used as the flash endpoint conditions, then additional calculations should be performed to predict working and breathing losses in accordance with the applicable API evaporation loss correlations.

Use of empirical correlations

The key advantage of using an empirical correlation to estimate a flash-gas factor, is that it minimizes the required user input information and eliminates the need to collect a pressurized liquid sample and have it analyzed. However, this is at the loss of some accuracy and the ability to predict the composition of the flash gases. Default flash-gas compositions are typically applied in these circumstances (e.g., to estimate CH₄, VOC and selected air toxic emissions such as benzene, toluene, ethyl benzene and xylenes [BTEX]).

Information requirements

The information requirements comprise the following:

1. Separator operating temperature and pressure.
2. Sales Oil API Gravity
3. Storage Tank Gas Molecular Weight and Speciation Profile

Limitations

If the application conditions are outside the valid usage range of the selected correlation, then an alternative method should be selected to determine the flash gas factor.

In all cases, the user may specify conservative input data for application of the correlation and/or may specify a safety factor for application to the correlation predictions if warranted.

Available options

McCain, Spicey and Lenn (2011) provide an evaluation of various recent and established correlations for predicting petroleum reservoir fluid properties. There are many options that may be considered such as Vazques Beggs (VBE) (1980), Rollins, McCain and Creeger (RMC) (1990), and numerous other correlations. Each has its own range of applicability and accuracies, with the more current correlations

tending to offer improvements over earlier ones. Nonetheless, it is important to choose one that is valid for the conditions being considered.

Currently, the Valko and McCain (2003) correlation is perhaps the most widely used correlation for predicting flash-gas factors for pressurized crude oil or condensate dispensed to a production storage tank (or storage tank). This is due to its generally good accuracies and relatively wide range of applicability. The correlation requires information on the operating conditions (i.e., temperature and pressure) of the first upstream pressure vessel (referred to here as a separator) from which the oil is dispensed and the API gravity of the weathered sales product from the storage tanks.

The validated operating range of the Valko and McCain (2003) correlation is:

1. Separator Temperature: 1.7 to 90°C (35 to 194°F)
2. Separator Pressure: 83 to 6550 kPag (12 to 950 psig)
3. API Gravity of the stock tank oil: 6.0 to 56.8° API
4. Separator gas specific gravity: 0.561 to 1.237

The GOR of the flashed product entering the storage tank (or the flash-gas factor), k_F , is determined using the following relations:

$$k_F = \exp(\ln k_F)$$

Equation 10

Where,

$$\ln k_F = 3.955 + 0.83z - 0.024z^2 + 0.075z^3$$

Equation 11

Where,

$$z = \sum_{n=1}^3 z_n$$

Equation 12

Where,

$$z_n = C_{0,n} + C_{1,n}VAR_n + C_{2,n}VAR_n^2$$

Equation 13

And,

k_F Flash gas factor for the storage tank (scf of flash gas/bbl of storage tank oil).

z, z_n Calculation parameters (dimensionless)

C, VAR Correlation parameters (see Table 4).

Table 4: List of values for parameters C and VAR for Equation 12.				
n	VAR	C ₀	C ₁	C ₂
1	$\ln P_{SP}$	-8.005	2.7	-0.161
2	$\ln T_{SP}$	1.224	-0.5	0
3	API	-1.587	0.0441	2.29×10^{-5}

In Table 4,

P_{SP} pressure (psia).

T_{SP} Separator temperature (°F).

API API gravity of the storage tank oil (°API).

Sample calculations

A spreadsheet application for applying the Valko and McCain correlation is available with this guidance document.

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Glossary

- API Gravity
- An inverse measure (expressed in degrees) of a petroleum liquid's specific gravity. Hence, if a petroleum liquid is less dense than another, then it has a greater API gravity. Most values are in the range of 10° to 70°. The formula used to determine API gravity is:

$$\text{API Gravity } [^\circ] = (141.5/\text{SG at } 60^\circ\text{F}) - 131.5$$

Where, SG is the specific gravity of the fluid.

- Associated Gas
- Natural gas that was in contact with oil in the reservoir.
- Backpressure Valve
- A valve designed to control flowrates in such a manner that upstream pressure remains constant. This type of valve may be operated by a diaphragm, spring or weighted lever.
- Blanket Gas
- Storage tanks may be equipped with gas blanket systems to reduce vapour emissions (especially when the vapours are sour) and to ensure that oxygen does not enter the vapour space of the tank when it is connected to a flare system or vapour recovery unit. The blanket gas is usually fuel gas, but any other inert gas could be used (e.g., nitrogen or carbon dioxide).
- Storage tanks with gas blanket systems are usually connected to a flare or vapour recovery system, but in some cases (if the gas is not sour and the applicable regulations allow) the tank vapours and blanket gas may be released untreated to the atmosphere through a vent system.
- Condensate
- Hydrocarbon liquid separated from natural gas that condenses due to changes in the temperature, pressure, or both, and that remains a liquid at standard reference conditions.
- Controlled Emissions
- The emission rate that occurs from a target source when its installed control device is properly maintained and operating in accordance with design specifications.
- Closed Vent System
- A system that is not open to the atmosphere and is composed of piping, ductwork, connections, and, if necessary, safeguarding features, liquids removal equipment and flow inducing devices that transport gas or vapour from one or more emission points to one or more control devices.
- Crude Oil, Extra Heavy
- Crude oil having an API gravity below 10° (i.e., a density of greater than 1000 kg/m³).

Crude Oil, Heavy	- Crude oil having an API gravity below 22.3° and greater than or equal to 10° (i.e., a density greater than 920 kg/m ³ to less than or equal to 1000 kg/m ³).
Crude Oil, Light	- Crude oil having an API gravity greater than 31.1° (i.e., a density less than 870 kg/m ³).
Crude Oil, Medium	- Crude oil having an API gravity less than or equal to 31.1° and greater than or equal to 22.3° (i.e., a density greater than or equal to 870 kg/m ³ and less than or equal to 920 kg/m ³).
Crude Oil Battery	- A system or arrangement of tanks or other surface equipment receiving primarily oil from one or more wells prior to delivery to market or other disposition. An oil battery may include equipment for measurement, for separating inlet streams into oil, gas, and/or water phases, for cleaning and treating the oil, for disposal of the water, and for conservation of the produced gas. A tank battery may also include a glycol dehydrator and compressor for conservation of the associated gas production if the facility is within economic distance of a gas gathering system.
Crude Oil Group Battery	- A crude oil production facility that receives production from two or more oil wells by flow lines and features individual separation and measurement equipment with all equipment sharing a common surface location.
Emulsion, Oil	- A mixture of crude oil containing formation water in relatively stable suspension or dispersion that requires treatment before the oil and water will separate. This separation may be achieved using time and heat, chemicals (called emulsifiers or emulsion breakers) or electricity.
Entrained Gas	- Gas suspended in bubbles in a stream of liquid such as water or oil.
Field Gas	- Natural gas extracted from a production well prior to its entering the first stage of processing, such as dehydration.
Flash-Gas Factor	- The flash-gas factor is the amount of flash gas liberated per barrel of oil produced (e.g., scf/bbl of oil) when oil from a pressurized source is flashed to a particular set of conditions. For determining the peak instantaneous flash gas liberation rates, the flash gas factor is normally determined at the operating temperature and pressure (e.g., local barometric pressure) of the storage tank.

For the purposes of determining the total amount of flash gas liberated from the product, the flash gas factors (e.g., scf/bbl of oil) is determined at the reported RVP of the sales oil.

If the flash gas factor is determined by flashing the gas to standard conditions of 1 atmosphere and 60°F (e.g., in a laboratory), the result is referred to as flash GOR (e.g., scf/bbl oil).

- Flash Gas-to-Oil Ratio (GOR) - The gas factor (e.g., scf/bbl oil) determined by flashing a pressurized oil sample to standard end conditions of 1 atmosphere (101.325 kPa) and 60°F (15.6°C) (e.g., in a laboratory).
- Fully-Speciatiated Substance - A fluid or chemical mixture that has been adequately characterized in terms of its dominant constituents to allow prediction of the rheological and thermodynamic properties of the substance, and in terms of any trace constituents to satisfy the application-specific needs of the user. Trace constituents may be of particular interest or concern because of their market value, health-risk properties, adverse environmental effects, catalysing or inhibiting properties, etc. In reality, no substance is ever fully speciatiated; even a highly purified substance may contain hundreds or more trace constituents, most of which are of no consequence or concern at the concentrations they occur. For a fully-speciatiated fluid, the developed composition profile is normalized so that the mol and mass fractions of the quantitated components sum to a value of 1.
- Hazardous Air Pollutants (HAP) - These are substances that pose a risk to human health; they also are referred to as air toxics by USEPA.
- Heater Treaters - A process unit for separating gas, oil and water from emulsified well streams by gravity and enhanced means of breaking emulsions such as heating, chemical and/or coalescing sections.
- Lease Automatic Custody Transfer (LACT) Unit - An automated system for measurement and transfer of oil from the producer's tanks to the oil purchaser's pipeline without a representative of either party having to be present. A LACT Unit also normally monitors the BS&W content of the oil to ensure that the product meets sales specifications. If off-spec product is detected, the LACT Unit either terminates the product transfer or redirects the off-spec product back to a designated slop tank for subsequent re-processing by the treater or directly to the treater.
- PIG - A device inserted into a flow line with normal flow for the purpose of cleaning out accumulations of wax, scale and debris and into gas pipelines for the purpose of displacing liquids from the pipeline (e.g., water or condensate). The pig used in flow lines cleans the pipe walls by means of blades or brushes attached to it. The pig used in gas pipelines is usually a neoprene displacement spheroid.
- Produced Water - Water that is extracted from the earth from a crude oil or natural gas production well, or that is separated from crude oil, condensate, or natural gas after extraction.

Recycle System	- An automated system for drawing off-spec crude oil from the bottoms of tanks and pump it into the inlet line to the heater treater for reprocessing.
Reference Fluid	- A fluid having a composition and flowrate representative of the bulk fluid entering a pressure vessel located upstream of the production storage tanks. The reference fluid is used in process simulation calculations to predict the composition of the pressurized liquid being dispensed to the storage tanks for any operating conditions of interest. The reference fluid is defined by mathematically combining the composition and flowrate of the associated gas stream and the pressurized liquid stream leaving a vessel at a particular set of operating conditions. If the composition and flowrate of the pressurized liquid are unknown, then an approximate reference fluid may be defined by mathematically combining the composition and flowrate of associated gas and sales oil; this is only valid to do where the gas-to-oil ratio is high enough that flashing the approximated reference fluid is able to give back essentially the same associated gas composition and sales oil flowrate. Although, some adjustments of the approximated reference fluid may still be required to achieve a proper mass balance.
Reid Vapor Pressure (RVP)	- A measure of the volatility of a hydrocarbon liquid (i.e., crude oil and petroleum refined products) at 37.8°C (100°F) as determined by Test Method ASTM-D-323. Because of the presence of air in the vapour space within the test method's sample container, as well as some small amount of sample vaporization during the warming of the sample to the test temperature, the RVP differs slightly from the TVP of the sample at this temperature. ASTM-D-5191 may be used as an alternative method for determining RVP for petroleum products; however, it should not be used for crude oils.
Routine and Non-routine Tank Operations	Routine tank operations are operations in which all installed vapour control features the tank are active and functioning properly. Non-routine operations are situations where one or more of the installed vapour control features have been bypassed or are taken out of services. For a floating roof tanks, non-routine operations occur when the floating roof is damaged or it has been landed causing the vacuum breakers to open.
Scrubber	- A vessel used to knock out entrained droplets and/or dust particles in gas flow (usually having high gas-to-liquid ratios) to protect downstream rotating or other equipment or to recover valuable liquids from the gas. Scrubbers commonly are used in conjunction with dehydrators, extraction plants, instruments, or compressors.
Separator	- A vessel used to separate multi-phase flow into its constituent phases (e.g., gas, hydrocarbon liquid, water and solids) by gravity settling and/or centrifugal action. A separator may be either two-phase (e.g., gas/liquid), three-phase (e.g., (gas/hydrocarbon liquid/water) or four-phase (e.g., gas/hydrocarbon liquid/water/sand). Separators can have incidental added

heat, but if the heat added or removed is more than incidental then the vessel falls in the family of “heaters/treaters”.

Solution Gas	- Natural gas dissolved in crude oil and held under pressure in the oil in reservoir.
Standard Reference Conditions	- Most equipment manufacturers reference flow, concentration and equipment performance data at ISO standard conditions of 15°C, 101.325 kPa, sea level and 0.0 percent relative humidity.
Tank	- A device designed to contain liquids produced, generated, and used by the petroleum industry. Tanks are constructed of impervious materials, such as concrete, plastic, fiber-reinforced plastic, or steel, and are designed to provide adequate structural support for the intended contents, and satisfy specific pressure and vacuum limits as well as wind and snow loads. Design standards such as API 620 and 650 and API Specification 12B, 12D, 12F and 12P, establish the applicable design procedures and set default pressure and vacuum values in the absence of specific requirements by the purchaser.
Thief Hatch	- A hinged cover on an opening located on the top of the tank through which liquid sampling or liquid-level measurements are manually performed. The hatch features an integral safety device for pressure-vacuum relief or simply pressure relief, depending on the design of the safety device and the application requirements.
True Vapor Pressure (TVP)	- A measure of the equilibrium partial pressure exerted by a liquid at a specified temperature. The TVP of an organic liquid may be determined using Test Method ASM D 2879.
Trace Constituent	- A constituent of a chemical mixture that does not contribute substantively to the total mass of the mixture. Most trace constituents occur in extremely small quantities and have no impact on the properties of the mixture and, at the concentrations they occur, are of no interest or concern for other reasons (e.g., their market value, health-risk effects, adverse environmental impacts, catalysing or inhibiting properties, etc.). The relevance or importance of trace constituents tends to be application and concentration specific and is usually limited to a small subset of the total number of trace constituents present in a chemical mixture. Hence, usually only those trace constituents of interest are quantitated if any are quantitated at all.
Uncontrolled Emissions	- The emission rate that would occur in the absence of a control device or during periods when a control device is not operational.
Unintentional Gas Carry-through	- Natural gas can be unintentionally carried through to a storage vessel during a liquid dump event (e.g., due to gas entrainment caused by inefficient gas/liquid separation as a result of an undersized separator, or due to the formation of a vortex at the entrance to the liquid outlet line) or through a dump valve that is stuck in an open or partially-open position (<i>i.e.</i> , where a valve failed to properly reseal).

- Vapour Balanced Tanks - Vapour balanced tanks feature piping that allows the vapours to freely flow between the ullage space of individual tanks. This allows vapours to be exchanged between tanks that are filling and those that are being emptied at the same time.
- Vapour Recovery Tower (VRT) - A tall or elevated vertical separator installed immediately upstream of a storage tank; it is used to recover flash gas from oil at pressures slightly above local atmospheric pressure. Oil is dumped from a separator or treater into the VRT and flows by gravity from the VRT into the storage tank. Use of a VRT captures flash gas without risk of the vapours being contaminated with air, while greatly reducing the amount of flashing occurring in the storage tanks.
- Vapour Recovery Unit (VRU) - A specialized compressor package (e.g., rotary vane, rotary screw, vapour jet or eductor) designed to capture low-pressure wet-gas streams from oil and condensate tanks and compress the gas into the suction of a gas conservation compressor or into a low-pressure gas gathering system.
- Vortex Breaker - A device located on the outlet nozzle of a vessel or tank to prevent vortex formation.
- Weathered or Stabilized Petroleum Liquids - This is any product that has a true vapour pressure less than 76 kPa at 21.1°C if it is stored at ambient conditions, or at its storage temperature if the product is heated.

Appendices

The calculations presented in this section are for converting the results of laboratory analyses to a normalized and fully-specified composition profile for a gas or liquid sample.

Calculation of Mass Fractions from Mole Fractions

If the composition of a multi-component fluid is known in terms of the mole fraction of each component, then the mass fraction of each component may be calculated using the following relation:

$$x_i = \frac{y_i \cdot M_i}{\sum_{i=1}^{i=N} y_i \cdot M_i} \text{ for } i = 1 \text{ to } N$$

Equation 14

Where,

- x_i Mass fraction of component i.
- y_i Mole fraction of component i.
- M_i Molecular weight of component i.
- N Number of components in the mixture.

Calculation of Mole Fractions from Mass Fractions

If the composition of a multi-component fluid is known in terms of the mass fraction of each component, then the mole fraction of each component may be calculated using the following relation:

$$y_i = \frac{x_i/M_i}{\sum_{i=1}^{i=N} x_i/M_i} \text{ for } i = 1 \text{ to } N$$

Equation 15

Conversion of Analyses from a Wet Basis to a Dry Basis

The laboratory analysis results are typically, but not always, expressed on a dry (i.e., moisture-free) basis. If the results of an analysis are expressed on a wet basis then they may be converted to a dry basis by applying the following relation where the subscripts Dry and Wet denote dry-basis and wet-basis respectively:

$$y_{Dry_{H_2O}} = 0$$

Equation 16

$$y_{Dry_i} = \frac{y_{Wet_i}}{1 - y_{Wet_{H_2O}}} \text{ for } i \neq H_2O$$

Equation 17

Thus, it follows that,

$$y_{Dry_{CH_4}} = \frac{y_{Wet_{CH_4}}}{1 - y_{Wet_{H_2O}}}$$

Equation 18

And,

$$y_{Dry_{CO_2}} = \frac{y_{Wet_{CO_2}}}{1 - y_{Wet_{H_2O}}}$$

Equation 19

Conversion of Analyses from a Dry Basis to a Wet Basis

To convert a composition profile from a dry basis to a wet basis requires the dry composition and information regarding the amount of moisture present in the wet composition. Ideally, the moisture content should be a measured value; although, in some cases it may be reasonable to estimate the moisture content based on the saturation limit with respect to water and a known or assumed relative humidity value.

$$y_{Wet_i} = y_{Dry_i} \cdot (1 - y_{Wet_{H_2O}}) \text{ for } i \neq H_2O$$

Equation 20

Thus, it follows that,

$$y_{Wet_{CH_4}} = y_{Dry_{CH_4}} \cdot (1 - y_{Wet_{H_2O}})$$

Equation 21

And,

$$y_{Wet_{CO_2}} = y_{Dry_{CO_2}} \cdot (1 - y_{Wet_{H_2O}})$$

Equation 22

Calculation of the Average Composition of Multiple Samples

The average composition profile of multiple samples is determined using the following relation:

$$\bar{y}_i = \frac{\sum_{j=1}^{N_S} y_{i,j}}{N_S} \quad \text{for } i = 1, N_C$$

Equation 23

Where,

\bar{y}_i	Average mole fraction of component i determined from multiple sample analyses.
$y_{i,j}$	Mole fraction of component i in sample j.
N_C	Number of components.
N_S	Number of samples.

Correction of a Composition Profile to an Air-free Basis

A gas or vapour composition is corrected to an air-free basis using Equation 24, Equation 25 and Equation 26 in series. The first of these equations is presented below:

$$y_i'' = y_{Gas_i} - y_{Air_i} \cdot \left(\frac{y_{Gas_{O_2}}}{y_{Air_{O_2}}} \right) \quad \text{for } i = 1, N$$

Equation 24

Where,

y_i''	Mole fraction of component i in the target analysis expressed on an air-free basis (kmol/kmol).
y_{Gas_i}	Mole fraction of component i in the target gas analysis expressed on an air-in basis (kmol/kmol).
$y_{Gas_{O_2}}$	Mole fraction of O ₂ in the target gas analysis expressed on an air-in basis (kmol/kmol).
y_{Air_i}	Mole fraction of component i in the background air analysis (kmol/kmol).
$y_{Air_{O_2}}$	Mole fraction of O ₂ in the background air analysis (kmol/kmol).

The following equation should be applied to set any negative terms to zero.

$$y_i'' = 0 \text{ if } y_i'' < 0 \text{ for } i = 1, N$$

Equation 25

The air-free composition then is normalized using the following relation:

$$y_i'' = \frac{y_i''}{\sum y_i''} \text{ for } i = 1, N$$

Equation 26

A default air composition is presented in Table 5. Where concentration of a given component is reported as a range of values, the average of the range should be used. The term “Trace” shall be interpreted as meaning the value zero since the minimum detection limit of the applied analysis methods is not known.

Substance	Chemical Symbol	Molecular Weight	CAS No.	Mol Fraction	Normalized Mol Fraction
Nitrogen	N ₂	28.01344	7727-37-9	0.78084	0.7808187719
Oxygen	O ₂	15.99943	7782-44-7	0.20947	0.2094643053
Argon	Ar	39.9481	7440-37-1	0.00934	0.0093397461
Carbon dioxide	CO ₂	58.93320	124-38-9	0.350 × 10 ⁻³	0.0003499905
Neon	Ne	20.17976	7440-01-9	0.1818 × 10 ⁻⁴	0.0000181795
Helium	He	4.00260	7440-59-7	0.524 × 10 ⁻⁵	0.0000052399
Methane	CH ₄	16.04257	74-82-8	0.17 × 10 ⁻⁵	0.0000017000
Krypton	Kr	83.7982	7439-90-9	0.114 × 10 ⁻⁵	0.0000011400
Hydrogen	H ₂	2.01589	1333-74-0	0.53 × 10 ⁻⁶	0.0000005300
Nitrous oxide	N ₂ O	44.01287	10024-97-2	0.31 × 10 ⁻⁶	0.0000003100
Xenon	Xe	131.2936	7440-63-3	0.87 × 10 ⁻⁷	0.0000000870
Ozone ¹	O ₃	47.99829	10028-15-6	trace to 0.8 × 10 ⁻⁵	0.0000039999

Table 5: Default composition of dry air.					
Substance	Chemical Symbol	Molecular Weight	CAS No.	Mol Fraction	Normalized Mol Fraction
Carbon monoxide	CO	28.01021	630-08-0	trace to 0.25×10^{-6}	0.0000001250
Sulfur dioxide	SO ₂	64.0644	7446-09-5	trace to 0.1×10^{-6}	0.0000000500
Nitrogen dioxide	NO ₂	46.00558	10102-44-0	trace to 0.2×10^{-7}	0.0000000100
Ammonia	NH ₃	17.03056	7664-41-7	trace to 0.3×10^{-8}	0.0000000015

Source: Mackenzie, F.T. and J.A. Mackenzie (1995) **Our changing planet**. Prentice-Hall, Upper Saddle River, NJ, p 288-307. (After Warneck, 1988; Anderson, 1989; Wayne, 1991.). Web address: http://eesc.columbia.edu/courses/ees/slides/climate/table_1.html

¹ Low concentrations in troposphere; ozone maximum in the 30- to 40-km regime of the equatorial region.