

Refinery air emissions management

Guidance document for the oil and gas industry

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Executive summary

This document describes 'good practices' and strategies that can be used in petroleum refineries to manage emissions of air pollutants, and includes a special section on how to identify odour sources. Many of the techniques may also be applicable to those chemical plants and petroleum distribution facilities having similar equipment and operations.

Since individual refineries are uniquely configured, the techniques, which comprise a collection of operational, equipment and procedural actions, may not be applicable to every site. Applicability will depend on the types of processes used, the currently installed control equipment and the local requirements for air pollution control.

This document will assist plant personnel to identify those techniques which may be used to optimize the management of air emissions and to select appropriate techniques for further site evaluation.

The document is organized as follows:

- Introduction
- Developing emission inventories
- Sources and control of hydrocarbon emissions
- Sources and control of combustion emissions
- Odour control and management



Introduction

Air emissions overview

Petroleum refineries are complex systems of multiple linked operations that convert the refinery crude and other intake into useful products. The specific operations used at a refinery depend on the type of crude refined and the range of refinery products. For this reason, no two refineries are exactly alike. Depending on the refinery age, location, size, variability of crude and product slates and complexity of operations, a facility can have different operating configurations and significantly different air emission point counts. This will result in relative differences in the quantities of air pollutants emitted and the selection of appropriate emission management approaches.

For example: refineries that are highly complex with a wide variety of hydrocarbon products are likely to have more product movements and hence a potential for relatively higher fugitive, tank and loading emissions; refineries that process heavier or high sulphur crude and which have higher conversion are likely to have relatively higher combustion emissions because of their higher energy demand. Each refinery will have site-specific air pollution management priorities and unique emissions management needs as a consequence of all these factors. National or regional variations in fuel quality specifications can also affect refinery emissions as stricter fuel quality requirements will often require additional processing efforts.

Emission types

Refinery air emissions can generally be classified as either hydrocarbons, such as fugitive and volatile organic compounds, or combustion products such as NO_x , SO_x , H_2S , CO , CO_2 , PM and others. When handling hydrocarbon materials, there is always a potential for emissions through seal leakage or by evaporation from any contact of the material with the outside environment. Thus, the primary hydrocarbon emissions come from piping-

system fugitive leaks, product loading, atmospheric storage tanks and wastewater collection and treatment.

A refinery uses large quantities of energy to heat process streams, promote chemical reactions, and provide steam and generate power. This is usually accomplished by combustion of fuels in boilers, furnaces, heaters gas turbines, generators and the catalytic cracker. This results in the emission of products of combustion.

In addition to hydrocarbon losses and core combustion emissions, refineries emit small quantities of a range of specific compounds that may need to be reported if threshold limits are exceeded. Controls on core emissions may also be effective for these (e.g dust controls are effective for reducing emissions of heavy metals, VOC controls are effective for specific hydrocarbons such as benzene).

Potential emissions impacts

Management of refinery emissions is focused on meeting local and national standards. Air quality standards are expressed as concentration limit values for specific averaging periods or as the number of times a limit value is exceeded. The actual concentrations generated depend on the characteristics of specific site emission points and also on the local meteorological conditions. Emission limit standards may also apply where long range or regional pollution is of concern. Here, the details of the site emission are unimportant but the total site emission of certain pollutants may be subject to a national or regional emission reduction plan.

The purpose of air quality standards is to protect the human population from adverse impacts of pollution from all sources. The rationale behind specific standard values can be found in, for example, the technical documentation for the World Health Organization Air Quality Standards. Not all pollutant concentrations can be directly

linked to simple source emissions. NO_x and volatile organic compounds (VOCs) can react in the lower atmosphere under suitable conditions to create higher than natural environmental concentrations of ozone. A regional or national emission control plan is needed to regulate such episodic ozone events.

Understanding potential impacts of emissions

To better understand impacts, both ambient air quality monitoring and modelling is used. Dispersion modelling is sometimes conducted on specific emission sources to evaluate off-site potential concentrations. Using local meteorology (e.g. wind speed and direction) and details of the emission release (e.g. stack height, temperature and quantity), the location and magnitude of maximum concentrations can be predicted. Ambient air quality monitoring may be used to verify these predictions, especially if limit values are predicted to be approached, or to provide assurance that no breaches occur.

Regional air quality modelling can be used to evaluate the impact of multiple sources on background air quality.

Control scenarios

Regulatory agencies can specify air pollution emission limits and control requirements in a variety of ways. These include limits on the quantity of a pollutant that may be emitted, the allowable concentration of the emission, the resultant local ambient concentration, a target emission reduction and specific monitoring and repair procedures, etc. Sometimes, more than one of these emission limits and control requirements are applied to the same source. Guidance on emission control techniques may also be provided, for example information on effectiveness, cost and applicability.

Table 1 provides examples of the ways that regulatory agencies may control air emissions. In

Table 1 Examples of air emissions control scenarios

Scenario	Example control requirement	Example application
Pollutant emission quantity limit	Maximum tonnes/annum	<ul style="list-style-type: none"> Maximum quantity of SO_x, NO_x, PM from stack or site (site 'bubble' limit). Maximum hydrocarbon or toxics from vent.
Pollutant emission concentration limit	Maximum mg/m ³ in flue gas	<ul style="list-style-type: none"> Maximum ppm of SO_x or NO_x in flue gas. Maximum mg/m³ of PM on flue gas. Maximum ppm of hydrocarbon from vent.
Ambient concentration limit	Maximum micrograms/m ³ in ambient air	<ul style="list-style-type: none"> Maximum concentration of SO_x, NO_x or PM in ambient air.
Selected control	Agreed technology step or operational measure	<ul style="list-style-type: none"> Use of specific control equipment (e.g. SCR, wet gas scrubber (WGS), electrostatic precipitator (ESP), etc.). Application of specific rim seals on atmospheric storage tanks. Multi-seal pumps. Use of natural gas to replace liquid fuel firing
Specified control performance	Pollutant removal efficiency	<ul style="list-style-type: none"> Percent removal of PM and SO_x from catalytic cracker regenerator stack. Destruction efficiency for oxidation unit on a product loading system.
Specified control practice	Inspections and repair	<ul style="list-style-type: none"> Piping system component monitoring and leak repair. Monitoring of tank rim seals and floating roof gaskets.

most cases, the control scenarios are not unique. They are often copied from other countries that have well established national air pollution reduction programmes. It is also common that the more stringent control requirements tend to be propagated.

In many locations, facilities must apply what is often called 'best available technology' (BAT) and 'best environmental practice' (BEP). The definition of BAT and BEP can vary from agency to agency, but it generally refers to well-established commercially available control equipment, designs, principles or practices that are technically and economically applicable. The cost-effectiveness of implementing a specific control should be assessed, particularly where a retrofit to an existing unit is concerned.

Source pollutant emission limits

Regulating emissions by setting a limit on the total quantity (e.g. kilograms) of a pollutant emitted in a given time can obscure environmental performance because comparison of different facilities of different sizes or function is not easily made. It is preferable to set a concentration limit where the concentration is expressed at some standard condition. The limit can be set for an individual source, a group of similar sources or for the entire facility (i.e. a bubble limit). Typical applications of this type of limit are for SO_x, NO_x and particulate matter (PM) from combustion sources and for hydrocarbons from process vents or from product loading operations.

Source pollutant concentration emission limit

A concentration limit on the pollutant being released is typically defined as an average concentration over a given time period. Time periods may be hourly, daily, annual, depending on the pollutant in the stream being released. The concentration should be referenced to a given

dilution, for example, for flue gas stack concentrations this is usually 3% oxygen at 1 atm and 0 °C of dry flue gas vapour. It is important to use consistent units. In Europe, for stack gases (except CO) and dust, the concentration limit is expressed in units of mg/m³.

Ambient concentration limit

Care has to be taken over units for ambient air concentration limits because notation can be confusing, particularly if measurements are cited in volume units and the standards in mass units. Mass units are necessarily expressed at one atmosphere and 0 °C, and a µg/m³ scale is used. An averaging time has to be specified, and some standards have more than one period specified. Common periods are hourly, daily, annual. As a companion to the limit, and recognizing that concentrations in the atmosphere are highly variable, a certain number of limit exceedances may be allowed. The limit may be equivalently expressed as a percentile of suitably averaged concentrations rather than an overall maximum.

As discussed above, dispersion modelling can be used to perform an ambient air quality impact assessment to predict how the maximum expected concentrations from a source will compare to the ambient concentration standards. Ambient air quality monitoring can be used to inform on actual concentrations, especially where sources apart from a refinery, for example traffic, are present and dominant.

Specified control equipment

It is preferable that the refinery has flexibility in selecting from alternative methods of emission reduction where this is needed and feasible, rather than the regulatory agency requiring the use of specific emissions control equipment. In most cases, an alternate control that provides equivalent emissions reduction is allowed to be substituted for the specified equipment.

Specified control performance

In cases where the regulatory agency sets a specific control performance, it is usually expressed as the required removal efficiency of a specific pollutant from the discharged stream under normal operating conditions. Examples include PM and SO_x from catalytic cracker regenerator vents, and residual hydrocarbons from product loading emission control systems. Alternate control equipment or procedures are usually allowed as long as the percent reduction in emissions is achieved.

Specified control practice

In cases where the regulatory agency requires a specified practice to be applied, it is important that standard procedures are used and that the frequency of inspection is appropriate to the level of control required and reflects any demonstrated continuous improvement. Examples of these are monitoring and repair of piping systems (e.g. valves, flanges, pumps, etc.) for leaks and inspection and repair of atmospheric storage tank rim seals with excessive gaps.

Developing emission inventories

An essential part of any emission management programme is a representative assessment of current and projected emissions. The emissions inventory allows comparison of potential sources for control and provides a mechanism to quantify potential reductions. Emphasis should be placed on making the inventory complete and of high quality so that it is as representative of plant emissions as possible.

In this report, each of the sections on emissions controls is preceded by a brief discussion of the methods available for estimating emissions for that type of source. Detailed methods for estimating emissions are available in the references.

Sources

There are two general types of refinery emissions: hydrocarbons and combustion products such as SO_x , NO_x and CO_2 . Most of the major pieces of process equipment handling hydrocarbons at refineries do not emit any combustion products. However, the combustion sources such as heaters and boilers will typically emit air pollutants and greenhouse gases as well as small amounts of hydrocarbons (VOC) due to incomplete combustion.

Hydrocarbons

When handling hydrocarbons, there is always a potential for leakage through seals and by evaporation from any contact with the outside environment. Examples of leaking through seals include leaks from piping connectors, valves, compressors and pumps. Examples of sources of evaporation include atmospheric storage tanks, product loading, and wastewater collection and treatment.

Combustion products

A refinery uses large quantities of energy to heat process streams, promote chemical reactions,

provide steam, isolate and recover excess sulphur and generate power. This is usually accomplished by combustion of fuels, typically those generated on site such as refinery fuel gas and the coke deposited on cracking catalysts. Examples of combustion sources include furnaces, boilers, heaters, turbines and the catalytic cracker regenerator.

Some sources of combustion products are units operated to safely control hydrocarbon emissions and which do not normally supply useful energy for plant operations. Examples of these are flares and incinerators/thermal oxidizers.

Estimating methods

For most emission sources, there are several ways to estimate emissions. These have mostly been developed by regulatory agencies, e.g. the US Environmental Protection Agency (US EPA) and industry groups such as CONCAWE and the American Petroleum Institute (API). Methods requiring more detailed design and process operating data provide more representative emission estimates and usually require more effort to apply the more detailed input data. The choice of emission estimating method may be prescribed or may be an operator's choice but should be recorded. The choice of methods should be consistent with the objective of the emission inventory, the intended use, information availability, time allowed, and resource needs.

In order of increasing data requirements and calculation efforts, estimating methodologies include average emission factors, correlations, computer models and direct measurement. This is also the general order of obtaining more representative emission estimates.

Average factors

Industry average emission factors have been published for a wide range of source types (see

References) and are often used for initial inventories and until more representative and source-specific input data are available. Typically, these factors are used by multiplying the factor by an operating parameter, such as throughput or fuel combusted, to obtain the estimated emissions.

An example of industry average emission factors are those for NO_x emissions. In this case the factors represent the quantity of NO_x emitted for a quantity of fuel burned (tonne NO_x/GJ fuel fired). In the case of a single factor for NO_x, there is no consideration of specific equipment design or differences in specific operating conditions.

Improved NO_x emissions quantification can be obtained through direct measurement of the specific source. In some cases, equipment vendors provide equipment-specific estimates. Models based on limited source measurements have proved very reliable. For example, measuring NO_x emissions in a furnace under known operating rates may result in an emission factor that may reasonably be applied to other similar operating and similarly designed heaters.

Correlations

In some cases, many of the major design and operating parameters can be input to equations that attempt to provide more representative emission estimates. Theoretically, the more complex the correlation and the more operating variables it incorporates, the more representative the emissions estimate. This assumes that actual operating data are used and not the model defaults.

Correlations can also be developed semi-empirically using discrete monitoring campaigns (e.g. effect of load or fuel changes on NO_x emissions from a heater). More simply, fuel sulphur content can be used to calculate SO₂ emissions.

Correlations are widely used for estimating tank and wastewater treating emissions. As these

equations can be complex, they are typically used as part of a computer model.

Another set of correlations are those for estimating fugitive losses from piping components. In this case, measurements of local hydrocarbon concentrations at each component are converted to an emission rate. They are then aggregated to quantify the total plant emissions.

Computer models

A wide range of computer software is available which can be used to calculate almost all plant emissions as a labour-saving device. As with manual approaches, the accuracy of the emission estimate will improve as more source-specific input data is used.

The two most widely used emissions estimating computer programs are those for atmospheric storage tanks and wastewater treating. Versions of these are available from the US EPA (see *References*). The manual calculation methods for estimating emissions from these two sources are very tedious, and the use of computer models is recommended. Although significant equipment-specific and operating input data are required, the emission estimating results are widely accepted by regulatory agencies.

Measurements

The most representative way to estimate emissions is by continuous monitoring of important parameters. This can be a combination of stack measurement using in-situ continuous emission monitors (CEMs) or discrete sampling campaigns and monitoring of fuel consumption from which flue gas volume flow at standard dilution can be assessed. Continuous monitoring of oxygen concentration is needed both for this step and for efficient combustion control.

CEM devices are useful for determining NO_x, SO₂, CO concentrations and for monitoring changes in

dust. Manual sampling is still needed for calibration purposes, especially for dust where a CEM device cannot measure concentrations directly. CEMS are best applied to the largest sources (e.g. combustion systems > 100 MWth) .

As described above, measurement can be combined with correlation techniques to parameterize the performance of furnaces (e.g NO_x emissions) where there are defined changes in, for example, load or fuel mix in the case of dual-fired systems.

It is important to recognize that continuous monitoring is not synonymous with continuous measurement as not all inputs need to be determined with the same frequency in order to calculate emissions.

Quality assurance

The inventory of emissions to air is a key component of a refinery environmental management system (EMS). The support and active involvement of senior management is needed to provide the resources for the inventory activity and to ensure proper evaluation and review of the results.

The principal quality assurance steps are to ensure that the methodology used to quantify emissions from each source is adequately documented and that results are reviewed on a regular basis.

Transparency is very important especially where inventory results are used interactively in refinery management, for example in verifying compliance with refinery bubble limits or for demonstrating continuous improvement in reducing emissions which can assist decisions on the frequency of leak detection and repair programmes.

Where specific inventory results are required for regulatory reporting purposes the EMS should ensure that the internal methodologies are consistent with reporting requirements.

In many refineries necessary data for the inventory is gathered and held in the refinery data collection system. Automated links to the data collection system for such key data can usefully support the inventory effort.

Guidelines on auditing an inventory are given below.

Good practices for emissions inventory development

- Check that all emissions sources are included in inventory.
- Use the most appropriate estimating methods and follow the application guidance.
- Collect representative equipment design and plant operating input data.
- Emphasize the need for inventory results that are representative of operations.
- Ensure continuity of personnel skills, experience and knowledge.
- Conduct an independent review of the inventory development and results.
- Address deficiencies found in review and consider recommended improvements.
- Document all assumptions and methodologies used.

Auditing an emissions inventory

The complexity of collecting operating data and using various methods to obtain emissions estimates introduces many opportunities for improvements over time. Conducting a systematic audit of the emissions inventory development process can identify potential improvement areas, check calculation methods, minimize errors and provide recommendations for results that are more representative of actual plant emissions.

Whenever possible, audits should be conducted by specialists with extensive experience in

applying and developing emissions estimating techniques. The more knowledgeable and experienced the auditors, the more likely the results will be meaningful. Audit teams should also include plant personnel for training purposes as well as for their knowledge of the facility and current practices.

Review procedures

The primary focus of an independent review is to confirm the quality of the inventory and to identify any errors or omissions in inventory development. Evaluating estimating methods and the input data are essential parts of the review process. During the review, all input data are checked for reasonableness.

The first step in reviewing the emissions inventory is identifying how the inventory will be used. Often, there are several uses for the inventory including regulatory reporting and corporate emissions tracking. Knowing the reasons that the inventory was developed will help guide the reviewers in identifying appropriate recommendations for improvement.

Initially, a check of all potential emission sources consistent with the emission inventory purpose is made. All calculation models and factors used to estimate emissions are checked to confirm that they are appropriate for representing the sources and are being used correctly.

All assumptions and input data should be thoroughly reviewed. The quality of the inventory will depend on the quality of the specific plant operating data. Checks should be made to make sure that all assumptions are reasonable and are fully documented. Improvements to improve accuracy should be recommended.

Checklist

To ensure that all emission estimating procedures are reviewed, a preliminary list of emission inventory pollutants, sources and items to check is developed. The source lists are the most critical items to develop correctly and sufficient time should be allocated to making sure that all appropriate sources are included in the inventory.

Input data for calculating emissions from each source is checked with emphasis on the methodology used and the input data quality. The validity of the detailed input data is checked and confirmed to be representative of actual. This includes a review of all the details of how the data are used in obtaining an estimate of the emissions.

Documentation for all assumptions made to complete the inventory is confirmed. Improvements to improve accuracy should be recommended.

Reporting results

Documentation of the results and recommended improvements is as important as doing a thorough review of the estimating procedures. The audit is of limited value if the issues raised are not clear and the plant is not able to implement the recommendations.

Audit findings will fall into two general areas: items where there are errors that need to be corrected, and items where improvements may be made to make the estimate more representative. Where the current estimating procedure is adequate, quality and accuracy may be improved and the recommended improvement(s) may be considered for use at the next emission inventory update.

Documentation should include the emission source, the issue that needs to be addressed and specific recommendations on how to proceed with follow-up. The recommendations should have sufficient detail so that plant personnel can implement them.

Sources and control of hydrocarbon emissions

The primary sources of hydrocarbon emissions are leaks from piping system components, evaporation from product loading, losses from atmospheric storage tanks and evaporation from wastewater collection and treatment. The relative emission quantities from these sources might appear as provided in Table 2.

This represents a refinery with good tank management (appropriate storage of volatile material in floating roof tanks, appropriately equipped tanks) and avoiding unnecessary discharges of hydrocarbons to the wastewater treatment system. Adding vapour balancing and vapour recovery systems for product loading can significantly reduce this contribution. Fugitive emissions from equipment leaks present a continual challenge.

Fugitives and piping systems

Refineries typically contain hundreds of thousands of piping components such as valves, connectors, flanges, pumps and compressors. Each of these has the potential for the process fluid to escape around the seal into the environment. While the quantity of emissions from each individual component is usually very small, the large number of components in a refinery may make fugitive emissions the largest aggregate source of hydrocarbon emissions.

Studies have found that while almost every component has a very small leak rate, more than 80% of emissions typically come from a small population of the components that are considered 'high' leakers. Finding and fixing these larger leaks should be a priority and is the driver for a leak detection and repair programme.

Leaks are not usually visible. They have typically been found through the use of sensitive gas sampling devices to 'sniff' for ppm concentrations

Table 2 Relative emission contribution for hydrocarbons

Source	Relative %
Fugitive equipment leaks	40–50
Product loading*	30–40
Storage tanks	10–15
Wastewater collection and treatment	10–15

*Without vapour control

on the piping component. As the 'sniffer' has to be very close to the leak site this is labour-intensive process. New optical gas imaging equipment can visualize leaks and make detection simpler and much more cost-effective. These techniques are discussed later.

Because fugitive piping system emissions are a potential large contributor to refinery hydrocarbon emissions, a number of controls have been developed and successfully applied. These fall into three general areas: improved seals; improved materials and metallurgy; and finding and repairing the large leakers. Some trade-offs can be made between these. For instance, using better designs and equipment can reduce maintenance costs. However, all successful fugitive control programmes will include some monitoring and repair.

Table 3 lists the most common controls for fugitive emissions and their relative costs.

These controls are discussed in more detail in the following sections. The most effective results are obtained when several control methods are applied. For example, if improved valve packing and pump seals are installed, the monitoring and repair programme can be conducted more cost-effectively. If low emission control valves with dual packing sets are installed, then leak monitoring of these components can be done much less frequently.

Table 3 Controls for reducing fugitive emissions

Emission control	Relative cost
Initiate a component leak detection and repair (LDAR) programme	Low/medium
Install improved packing in block valves	Low
Optimize valve stuffing box and stem finishes	Low
Install second valve, cap or plug on open-ended lines	Low
Use low emission type control valves	Medium
Upgrade pump seals	Medium
Use low emission quarter-turn valves	Medium
Use leakless technology (bellows valves; canned and magnetic drive pumps)	High

How to quantify emissions

The quantity of fugitive emissions is obtained by determining the emission from each piping system component in the refinery and summing these emissions to obtain the refinery total. There are many ways to determine the individual component emission rates. The simplest, and potentially least representative or least accurate, is to use industry average emission factors for each component type. If a periodic monitoring and component repair programme is conducted, a reduction of 75% for control efficiency can be applied to this number. If a more representative and accurate estimate of fugitive emissions is desired, the ppm readings from the monitoring programme gas detection instrument can be used in correlation equations to calculate the mass emission rate for each component. There are finite leak rates generally applied even when the detection instrument reads zero for the background concentration. There are numerous publications that provide guidance for estimating fugitive emissions, including the '1995 EPA Protocol' (US EPA, 1995a) and a calculation manual from the American Petroleum Institute (API, 1998b).

Open-ended lines

Open-ended lines—pipelines with a single valve preventing loss of fluid to the environment—should be avoided.

The recommended control for open-ended lines is to use a second valve, a plug or a cap at the end of the line. Valves on small bore sampling lines should be maintained.

Pump, compressor and valve stem sealing

In pumps, compressors and rising stem valves, there are shafts that pass through the device, between areas containing pressurized process fluid and the surrounding environment. These provide a potential path for process fluid to leak from the pump, compressor or valve. Various seals are used to minimize the quantity of leakage. A proper choice of sealing system can significantly reduce potential emissions. Numerous vendors can provide designs with excellent sealing performance. Use of superior sealing systems will often reduce field emissions control maintenance costs.

Pumps using mechanical seals may be of a single-seal or multi-seal design. The choice of design will depend on the specific gravity of the process fluid and on the desired level of emissions control. Design selection may sometimes be balanced against the cost of an emissions monitoring programme. The seals incorporate both rigid and flexible elements that maintain firm contact at the sealing interface, allowing the rotating shaft to pass through a sealed case while minimizing leakage of

the process fluid. The elements can be both hydraulically and mechanically loaded with a spring or other device to maintain firm contact with the rotating shaft.

A single mechanical-seal pump is the most economical choice and can often provide adequate emissions control provided that the seal face design and materials are appropriately chosen. Seal face materials should have a high modulus of elasticity, superior heat transfer properties and a low coefficient of friction. Since seals use the process fluid to lubricate the seal faces, there is potential for emissions of the process fluid. A single mechanical seal can also include a closed vent system that captures any leaking process fluid and returns it to the process or to a control device.

Dual mechanical seals provide excellent control performance with near zero emissions. There are two basic types of dual-seal systems: double-seal and tandem-seal systems. In a double-seal arrangement, a non-regulated barrier fluid between the seals is at a higher pressure than the process pressure. Leaks of process fluid into the barrier fluid are, therefore, prevented. In a tandem-seal arrangement, a non-pressured barrier fluid is used and, although process fluid can leak into the seal fluid, a collection system can be incorporated to remove and capture any process fluid that leaks.

Emission controls for centrifugal compressors require the use of mechanical seals equipped with a barrier fluid and controlled degassing vents or enclosure of the compressor seal and venting of leakage emissions to a control device. Seal designs can be labyrinth, carbon ring, bushing, circumferential or face seals. Combinations of seal types in a single compressor are typical. Seal systems can use liquid buffer fluids (wet seals) or gas buffer fluids (dry seals). With oil wet seals, there is usually a need for systems to remove the barrier oil from the process gas.

A labyrinth seal design incorporates a complex path for the process fluid, making it difficult for the fluid to pass through and thus creating a barrier to help prevent leakage. Such a design typically includes multiple paths or grooves spaced tightly so that there is high resistance against escape of the fluid. To be effective, very small clearances are required between the labyrinth and the running surface. Labyrinth seals on rotating shafts provide a non-contact sealing action by controlling the passage of fluid through a variety of chambers by centrifugal motion. At higher speeds, centrifugal motion forces the liquid towards the outside and therefore away from the passages. Process gas is trapped in the labyrinth chamber preventing its escape. When leakage of process gas must be prevented, a buffer fluid is injected between the labyrinths. Labyrinth seals are often utilized as end seals with other mechanical seal designs. Over time, the emissions control effectiveness of a labyrinth seal may decrease due to wear and changes in spacing alignment.

Other seal designs are generally applicable to higher pressure applications than labyrinth designs. A buffer fluid is injected between the ring sets to prevent leakage. Leakage is dependent on seal size, compressor speed and process pressure. These seals use a fluid buffer which may leak into the process gas and also into the environment. Systems may include automatic shutdown if the buffer fluid pressure is lost.

Controlling emissions from reciprocating compressors requires minimization of gas leakage along the cylinder rod. This may be accomplished using appropriate packing systems on the rod and pressurizing the packing box.

Pump and compressor seal designs should be specified by the plant rotating equipment specialist after consultation with the plant environmental staff. Vendor reliability and experience with low emission requirements is critical.

There is a wide variety of packing designs and materials available to control leakage along a valve stem. Packing is installed in a stuffing box surrounding the valve stem and maintained under mechanical pressure to prevent the escape of process fluid along the stem or through the stuffing box. The mechanical pressure is provided by a screw or nut forcing a flange to compress the packing. Newer packing materials are typically graphite or polymeric. The polymeric materials often provide better emissions control performance but may not pass fire safety testing requirements.

Some valve packing is appropriate for factory installation in new equipment, and some is more appropriate for field packing replacement. Typically, preformed solid ring packing is for factory installation and continuous spool packing, cut in the field, is typical for repairs. Some preformed ring packing is provided pre-cut or can be field cut for repair applications. Some manufacturers may provide unique shapes to a packing in an attempt to improved emissions control performance.

For rising stem block valves, a basic packing set, consisting of three die-formed graphite sealing rings with two braided end rings to prevent packing extrusion, has been shown to provide good emissions control performance. Some manufacturers have incorporated the performance of both sealing rings and end rings into a spool-type packing for field repairs.

Use of more than five rings does not typically improve emissions control performance and may, in fact, reduce the pressure on some of the sealing rings allowing higher emission rates through the stuffing box. Some old valves may have very deep stuffing boxes allowing many extra packing rings. Spacers should be used in these to reduce the number of packing rings required to no more than five to seven.

In applications where valves are cycled frequently, such as control valves, dual packing sets with leak detection between the packing sets will provide better emissions control. In addition, 'live loading' using springs may be utilized to maintain constant pressure on the stuffing box.

Valve leakage can often be eliminated by tightening the screws or nuts on the flange to increase pressure on the packing in the stuffing box. Care should be taken so that the screws are not tightened to the point that the valve becomes inoperable. When tightening screws or bolts no longer reduces emissions, it is usually a sign that the packing or valve needs to be replaced.

Enhanced sealing techniques

In some situations, the leak may be repaired by injecting a sealing liquid directly into the stuffing box. This technique may be useful for emissions control if the leak is large and the valve cannot be removed from service for repacking or repair. Use of this technique should be done **after** technical evaluation as the technique may cause damage to the stuffing box and an additional path for emissions, and is not appropriate for all valves, valve types or service (e.g. valves that are likely to see more than occasional usage).

Quarter-turn valves typically provide lower emissions and maintenance compared to rising stem valves. These types of valves have been applied more in chemical plants than refineries. Prior to using this type of design, the plant mechanical equipment specialist should be involved in discussions with the vendor.

Most valve and packing suppliers will be able to provide results from testing their products for low emissions. There are several tests available and comparison between vendors may be difficult. Many vendors offer guarantees for various leak levels. What they are really offering is a lower probability that, over time, the valve will leak. It is

sometimes advantageous to purchase a better performing valve and packing system to reduce the need for costly field maintenance later.

Valve packing should be specified by the plant mechanical equipment specialist after consultation with the plant environmental staff. Vendor reliability and experience with low emission requirements is critical.

Valve quality: materials and finishes

In rising stem block valves, as the stem rises through the packing, there is potential for the stem to cause damage to the packing and hence create a path for increased emissions. The stem must be maintained in a clean and good condition to minimize this damage. The stuffing box finish must also be addressed as the packing can be damaged by a rough surface as it is lowered into the box, possibly creating a path for process fluid leakage.

To reduce the likelihood of packing damage as the valve stem is raised and lowered, it is important to keep the stem clean, straight and corrosion free. Choosing stem materials appropriate for the process application will help reduce corrosion. It is typical to find leaks from valves with corroded or damaged stems.

Stem and stuffing box finish is also important as there is a balance between packing damage as the stem is moved or the packing is installed and the ability of the packing to seal against the walls of the stuffing box and the stem. Too smooth a finish may not necessarily be beneficial. Material and finish should be selected after discussion with the plant mechanical equipment specialist and the valve and packing supplier.

Valve stems should be kept clean to avoid damage to the packing as the valve is operated. Cleaning with a dry soft cloth is recommended before the valve is turned. Use of grease on valve stems is not recommended since it may attract debris and result in packing damage.

'Leakless' components

In general, use of good seals and component designs in combination with a periodic leak detection and repair programme can provide emissions control almost equivalent to that of 'leakless' designs. The significant increase in costs to apply 'leakless' equipment is normally not warranted. In addition, the failure modes of 'leakless' designs can result in significant releases of process fluid, making them somewhat less effective in overall emissions control.

Leakless components are those that do not incorporate any leak paths between the process fluid and the environment. Seal-less pumps are designed without a shaft penetrating the pump housing. These may be diaphragm, canned or magnetic drive designs. Bellows seal valves have a welded sealed bellows between the process fluid and the environment to prevent emissions.

Even 'leakless' components can fail, and a means of monitoring is usually provided to detect such failure. In diaphragm pumps, holes may develop in the diaphragm. In canned or magnetic drive pumps, the casing may develop leaks. In bellows seal valves, the bellows may crack or the edge may separate allowing leakage of fluid. On bellows seal valves, a back-up packing system is usually installed to address this failure. Although in many locations emissions from components with 'leakless' design are assumed to be zero, in some locations a finite leak rate, usually equal to that from an uncontrolled flange, is applied.

Leakless technology should be considered in applications dealing with highly toxic process fluids or if there is a potential for release of highly odorous materials. The need for mitigation measures in the event of seal failure should be considered in these cases.

Leak detection and repair

The most effective fugitive emission control method is to conduct periodic surveys to find and repair leaking components. These surveys are commonly referred to as 'leak detection and repair' (LDAR), 'monitoring and maintenance' (M&M) or 'inspection and maintenance' (I&M) programmes. Each of these has two parts. The first part is to find the leaking components. The second part is to repair or replace the leaking components so that they are no longer hydrocarbon emission sources.

Even with the use of excellent sealing equipment, there will be some, but perhaps fewer, leaking components, and a monitoring programme will identify these for repair. Emission reductions of 50–90% have been demonstrated by LDAR programmes and, in some cases, the cost of the programme is more than compensated for by the value of the material no longer emitted from the leaking components.

Fugitive leaks occur randomly, and it is essentially impossible to predict which specific components will leak. Therefore, all components selected for inclusion in an inspection programme need to be monitored. The critical parameters in conducting an LDAR programme are the choice of components to include, the frequency of monitoring and the leak level above which component repair is required. There is also an option to apply optical gas imaging which is a more cost-effective monitoring methodology than the traditional 'sniffing' procedure (see below).

It is not necessary to include all component types in the monitoring programme. Emissions from components in heavy liquid service (kerosene and heavier) have been found to leak much less than components in gas or light liquid service and are, therefore, usually excluded from LDAR programmes. It is not economically justifiable to monitor these heavy liquid components because of the very small emission reduction that can be

achieved. Also, many LDAR programmes do not include flanges since their low relative leak rate and high number make them uneconomic to monitor. However, once LDAR has been applied to other components such as valves, open-ended-lines, pumps and compressors, leaks from flanges become a much larger fraction of the remaining fugitive emissions, and including them in the LDAR programme, at longer time intervals, may become justified if further emission reductions are required.

The sooner a leak is found and repaired, the less process fluid will enter the environment. There is a balance, however, between the cost of more frequent monitoring and the value of the material lost or its impact on the environment. Many LDAR programmes are conducted annually. In some locations, however, there is a requirement to monitor more frequently, especially when there are high percentages of leaking components. Sometimes, quarterly monitoring is required if more than 2% of components are leaking. However, there is also the opportunity to monitor less frequently if the percentage of leaking components is lower. Therefore, there is an incentive to use components which are of high quality or improved design to achieve lower leak percentages, and hence be allowed to monitor less frequently.

The most widely used monitoring method is the US EPA Reference Method 21. This is known as 'sniffing' and uses a sensitive gas-sampling instrument to measure the concentration of hydrocarbon adjacent to a potentially leaking component. Each component is monitored individually, as shown in Figure 1.

Guidelines for conducting Method 21 monitoring have been developed by the American Petroleum Institute (API, 1998a).

If the measured gas concentration is above a certain threshold, the component is considered a 'leaker'. This concentration was originally set at 10,000 ppm. Since the major contribution to

Figure 1 Leak detection: US EPA Reference Method 21

fugitive emissions is from the high leakers, setting a lower leak level for repair is not as good an emissions reduction approach as is finding and repairing the large leakers sooner.

If starting a new Method 21-based programme, annual monitoring of valves, pumps, compressors and open-ended lines in gas and light liquid service is recommended with a leak definition for repair of 10,000 ppmv. Including more components, conducting more frequent monitoring and lowering leak definitions for repair can be incorporated if additional fugitive emissions reduction is required.

With Method 21, each component must be monitored individually, so it is a very manpower-intensive activity. The process involves placing the probe of a hydrocarbon detection instrument at the potential leak surface of the component. Air and any leaked hydrocarbon are drawn into the probe and passed through a detector (flame ionization is the most widely used type of detector).

The instrument measurement in ppmv is correlated to the mass emission rate from the component, but

Figure 2 Leak detection: optical gas imaging

this is a relatively poor correlation. In practice, some large leaks may give lower relative readings and some small leaks may give higher relative readings depending on the nature of the leak. These are termed false negatives and false positives when they have an impact on repair decisions, and can result in the misapplication of repair activities.

The majority of fugitive emissions—typically more than 80%—come from a very small fraction of components with relatively high leak rates. Since most components do not leak at concentrations high enough to require a repair, most of the effort associated with Method 21 ‘sniffing’ is spent monitoring the non-leaking components.

A new method of component monitoring which uses optical gas imaging to detect leaks has been successfully applied at refineries and chemical plants around the world. Use of this technique is shown in Figure 2.

Optical gas imaging allows an instrument operator to easily view all components and detect leaking

The most widely used monitoring method is the US EPA Reference Method 21, also known as ‘sniffing’ (Figure 1), which uses a gas-sensitive instrument to measure the concentration of hydrocarbon adjacent to a potentially leaking component.

Optical gas imaging (Figure 2) enables the operator to visually detect leaking hydrocarbon gas, and allows leaks to be identified more quickly and at lower cost than the ‘sniffing’ method.

Figure 3 A leaking valve, viewed using optical gas imaging equipment



hydrocarbon gas in a real-time video image. Using this equipment, components may be viewed as shown in Figure 3, and leaks identified more quickly and at lower cost compared to using the 'sniffing' method.

The remote sensing and instantaneous detection capability of optical gas imaging allows an operator to monitor larger areas of a process unit much more efficiently, eliminating the need to measure the hydrocarbon concentration at each individual component. When using optical gas imaging to find leaks, all components showing evidence of hydrocarbon leakage are scheduled for repair.

The initial repair for valves found to be leaking is to tighten the packing gland to further compress the packing and seal the leak path. At locations that are just starting an LDAR programme, this technique has a very high success rate. If the gland tightening is not successful, then the next time the valve is out of service, the packing should be replaced with a new low-emission packing chosen after consultation with the plant mechanical equipment specialist and the packing vendor.

Flange repairs involve retightening of the bolts and replacement of the gasket when next removed from service. Pump and compressor repair should be coordinated with the plant machinery specialist. Equipment should be monitored after repair to ensure that the repair was effective in stopping the hydrocarbon leak.

Good practices for control of fugitive emissions

- Use low-leak multi-seal arrangements for pumps and compressors.
- Use low-leak dual-seal designed control valves.
- Use low-leak block valve packing and keep stem clean.
- Consider use of quarter-turn valves where appropriate.
- Install a second valve, a plug or a cap on all open-ended lines.
- Using available techniques such as the optical gas imaging camera in combination with 'sniffing' according to Method 21, perform annual leak detection and repair on gas and light liquid valves, pumps, compressors and open-ended lines.
- Repair or replace leaking components.

Storage tanks

Atmospheric storage tanks are utilized in a refinery for a variety of hydrocarbon liquids including crude oils prior to processing, products waiting for shipment and intermediate streams. There are two general types of atmospheric storage tanks: fixed roof tanks and floating roof tanks. There are three types of floating roof tanks: external floating roof, internal floating roof and covered (or domed) floating roof. Typically, lower vapour pressure liquids such as heating oils and kerosene are stored in fixed roof tanks. Crude oils and lighter products such as gasoline are stored in floating roof tanks.

A fixed roof tank consists of a shell and a fixed roof with a gas space above the liquid surface, which is vented to the atmosphere through a pressure relief device. Some of the hydrocarbon liquid in the tank evaporates into the gas space and, when the tank is filled and the gas is expelled through the pressure relief device, this vaporized hydrocarbon is emitted. This is called 'filling loss'. A small amount of gas is also released due to daily changes in atmospheric pressure and temperature. This is called 'breathing loss' or 'standing loss'. Typically, filling losses constitute 80–90% of the total losses for fixed roof tanks.

Floating roof tanks consist of a shell and a roof that floats on the hydrocarbon liquid. In the case of an external floating roof, the top of the floating roof is open to the environment. In the case of an internal or covered floating roof, there is a gas space between the floating roof and the roof on the top of the tank. The internal floating roof and covered floating roof tanks resemble a fixed roof tank with a floating roof placed internally on top of the hydrocarbon liquid.

In floating roof tanks there is a rim seal that reduces the quantity of hydrocarbon vapours passing through the space between the floating roof and the shell. There are also a number of roof 'fittings', which are openings in the floating roof, that provide for inspection and maintenance as well as sampling of the liquid.

With floating roof tanks, the hydrocarbon liquid evaporates and vapours can pass around the floating roof rim seal and also around openings for fittings in the floating roof. This is called 'standing loss'. In addition, a small amount of material can coat the shell and any vertical poles when the tank roof is lowered. This material evaporates and is called 'withdrawal loss'. The quantity of loss for floating roof tanks depends on the rim seal design and emission controls on the roof fittings.

Emissions from internal and covered floating roofs are much lower than for external floating roofs due to the elimination of wind driven pressure differences across the roof. Most of the emissions from floating roof tanks are due to standing losses.

Table 4 describes the most common controls for reducing tank emissions and their relative costs. For fixed roof tanks, the primary focus is on the collection of hydrocarbon vapours that are expelled when the tank is being filled. A standard approach is known as 'vapour balancing', where the vapour exiting the tank is sent to the space created where the liquid is coming from. This works well if the liquid is being offloaded from a nearby vessel, truck or another fixed roof tank. There are vapour transporting and safety issues that need to be addressed with this control option. However, vapour balancing can work well if the receiving vessel is situated close enough that costs for the necessary ducting and blowers are reasonable.

Vapours expelled from a fixed roof tank can also be collected for recovery or destroyed. Recovery is generally only used for very high value products and its application has typically not been for emissions control purposes. Recovery and destruction are the most costly controls and are discussed in more detail in the section on *Product loading* (page 26).

If the emissions from a fixed roof tank are significant, the material might be better stored in a floating roof tank. If a floating roof tank already exists, costs may be moderate depending on available piping and current use of the floating roof tank. Alternatively, the fixed roof tank can be converted into an internal floating roof tank, but costs to do this are relatively high.

In floating roof tanks, emissions are mostly due to standing losses which come from vapour passing the rims and roof fittings. A first step in emission reduction is to ensure that the controls on these are in good condition. Roof fitting gaskets and wipers

Table 4 Controls to reduce storage tank emissions

Tank type	Emission control	Relative cost
Fixed roof	Install vapour balance system	Medium
	Use existing floating roof tank	Site specific
	Install internal floating roof	High
	Apply vapour destruction	Very high
	Apply vapour recovery	Very high
External floating roof	Check and repair roof fitting gaskets	Low
	Check and repair existing rim seals	Low
	Install secondary rim seal	Medium
	Change rim seal to mechanical shoe seal	High
	Convert to covered floating roof tank	High
Internal floating roof	Check and repair roof fitting gaskets	Low
	Check and repair existing rim seals	Low
	Install secondary rim seal	Medium
	Change rim seal to mechanical shoe seal	High
	Apply vapour destruction	Very high
	Apply vapour recovery	Very high

should be checked to ensure that they are in good condition and are providing a proper vapour seal. The rim seals should be inspected for excessive gaps. If none exist, a secondary rim seal can be installed to reduce the vapour losses across the primary seal. If a vapour mounted primary seal is being used, this can be changed to a mechanical shoe primary seal with a secondary seal. This combination will provide excellent vapour control performance for the rim emissions.

If additional emissions reduction is needed, external floating roof tanks can be converted to covered floating roof tanks, which will eliminate the wind driven emissions. This option is relatively expensive but is sometimes justified by product contamination issues (e.g. eliminating rainwater) in addition to emissions reduction needs.

In extreme circumstances, usually for very odorous or toxic liquids, an internal floating roof tank may require collection of the vapours and use of vapour recovery or destruction. However, in these cases, use of a closed pressurized vessel may be more appropriate than an atmospheric storage tank.

The controls mentioned above are discussed in more detail in the follow sections. Options should be reviewed with the site tank specialist and vendors should be contacted to discuss locally available options and equipment. The most effective results for floating roof tanks are obtained when several of the controls are applied. For example, when both improved rim seals are used along with gaskets and bolts on roof fittings.

How to quantify emissions

The methodology for estimating tank emissions is complex. A set of semi-empirical equations based on laboratory tests on different seals and fittings has been developed by the American Petroleum Institute (API, 2002/03) and has been adopted by the US Environmental Protection Agency (US EPA, 1995b). Use of these equations for estimating tank emissions requires many inputs including the tank type, details of design, construction and operation and properties of the stored hydrocarbon liquid.

Typically, a spreadsheet is developed or a standard computer program such as the EPA's *Tanks* (US EPA, 2010) is used for the calculation. Hydrocarbon emissions from atypical operations such as floating roof landings and openings for tank cleaning also need to be included.

Tank types: fixed and floating

The design and emissions mechanism differences of fixed and floating roof tanks were discussed above. The floating roof can be an emission control for the fixed roof tank design. It reduces contact of the hydrocarbon liquid with the gas which is then expelled. The gas has a lower concentration of hydrocarbon vapour since it is not in constant contact with the liquid. In many locations, higher volatility liquids such as crude oil and gasoline must be stored in floating roof tanks to reduce emissions.

There are generally two types of floating roof tanks: internal floating roof and external floating roof. An internal floating roof tank is similar to a fixed roof tank with the placement of a floating roof inside. The external floating roof tank has the roof subject to the environment; to wind and rain. Hydrocarbon emissions from an internal floating roof tank are usually much lower because the wind-driven evaporation is limited by the fixed roof.

Sometimes, internal floating roof tanks are distinguished between internal floating roof and

covered floating roof. The internal floating roof then refers to tanks that were originally designed as internal floating roof tanks, often with less concern for losses from rim seals and roof fittings due to the expected presence of the fixed roof on the original design. They typically have riveted deck seams, no secondary rim seal and less control on the deck fittings.

A covered floating roof tank often refers to a tank that was originally designed as an external floating roof tank that then had a fixed roof installed. The floating roof construction is often quite different as the deck seams are usually welded rather than bolted and better seals are placed on the rim and roof fittings.

Floating roof rim seals

Floating roofs are designed to have an annular space between the perimeter of the floating roof and the tank shell to allow easy vertical movement of the roof as liquid is added or removed. As a fully open space would allow significant evaporation of liquid, the annular space is closed using a rim seal system.

There are many types of rim seal combinations and some unique vendor designs. Effective rim seal systems provide good closure of the annular space, accommodate irregularities in the tank shell and help the floating roof stay centered in the tank while allowing easy vertical movement of the floating roof.

Rim seal systems can consist of a primary rim seal and a secondary rim seal. For most internal floating roof tanks, a secondary rim seal is usually not necessary because the fixed or domed roof limits evaporation caused by the wind. For external floating roof tanks, secondary rim seals are usually recommended, depending on the volatility of the liquid stored.

There are three general types of primary rim seals: vapour-mounted, liquid-mounted, and mechanical shoe. Vapour-mounted and liquid-mounted primary

seals are typically made of non-metallic materials and are often foam filled. They resemble a sausage-shaped tube or envelope that is fastened around the outside circumference of the floating roof. Vapour-mounted primary seals have a vapour space between the liquid and the bottom of the seal. In liquid-mounted primary seals, the bottom of the seal touches the liquid. Both vapour-mounted and liquid-mounted non-metallic seals are vulnerable to damage from rivet heads and weld burs on the tank shell as the roof moves up and down, which can tear the fabric.

Liquid-mounted primary seals provide a much better emission control compared to vapour-mounted primary seals because the vapour space between the seal and the liquid surface is minimized. However, when torn, they easily become contaminated with liquid seeping into the interior of the seal. Therefore, it may be advisable to avoid the use of liquid-mounted primary seals so as not to have to deal with the contaminated seal when replacement is required.

A mechanical shoe primary seal uses light gauge metallic sheets that are formed together as a ring contacting the tank shell. These sheets are most often held against the shell by weights or springs attached to the floating roof. A seal fabric is connected between the top of the metal band and the floating roof to prevent emission of the evaporated liquid vapours contained above the surface of the stored liquid and below the fabric seal.

Mechanical shoe seals generally have a long service life and are not subject to the material integrity issues associated with non-metallic liquid- and vapour-mounted fabric seals. In addition, when paired with a secondary rim seal, mechanical shoe seals provide excellent emissions control performance. API has evaluated the relative emissions control of different rim seal combinations and provides detailed descriptions of their design characteristics (API, 2002/03).

Tables 5 and 6 provide comparisons of control efficiencies for different rim seal configurations. For external floating roof tanks, Table 5 shows the percent reduction in emissions from a single vapour mounted seal as a secondary seal is added or the seal is replaced with a mechanical shoe type primary seal and then a secondary seal is added. The table shows the superior performance of the mechanical shoe seal in reducing rim losses.

The mechanical shoe primary seal with a secondary seal is considered best technology for storing typical volatile hydrocarbons in external floating roof tanks.

For internal floating roof tanks, Table 6 on the following page shows the percent reduction from a single vapour mounted seal as a secondary seal is added or the seal is replaced with a mechanical shoe type primary seal and then a secondary seal is added. Similar to external floating roof tanks, use of a secondary seal or changing to a mechanical shoe

Table 5 Seal system impact on emissions from external floating roof tanks

Seal system configuration	Approximate control efficiency* (%)
Vapour mounted resilient primary rim seal	BASE
Vapour mounted primary rim seal with a secondary seal	60 – 70
Mechanical shoe primary rim seal	80 – 90
Mechanical shoe primary rim seal with a wiper seal	90 – 95
Mechanical shoe primary rim seal with a secondary seal	95 – 99

* Control efficiency is dependent on the size of the tank, the properties of store material, meteorological conditions and throughput.

Table 6 Seal system impact on emissions from internal floating roof tanks

Seal system configuration	Approximate control efficiency* (%)
Vapour mounted resilient primary rim seal	BASE
Mechanical shoe primary rim seal	50–60
Vapour mounted primary rim seal with a secondary seal	60–70
Mechanical Shoe primary rim seal with a secondary seal	70–80

* Control efficiency is dependent on the size of the tank, the properties of store material, meteorological conditions and throughput.

primary seal will result in lower emissions but the reduction will be relatively less because the fixed roof already provides significant emissions control.

Emissions for internal floating roof tanks are already lowered significantly by the fixed roof, hence rim seal improvements may not provide cost-effective reductions of overall tank emissions. In many cases, a vapour mounted primary seal provides adequate emissions control for an internal or covered floating roof tank.

To ensure good emissions control, it is important that, whichever rim seal system is used, it provides an effective closure of the annular space between the floating roof and the tank shell. Many locations require periodic inspection of these seals. Due to access constraints, inspections of internal floating roof tank seals are usually done visually rather than with hands-on physical inspection.

For internal floating roof tanks, the seals may be inspected through a hatch opening in the fixed roof. For external floating roof tanks, inspection may include measurement of gaps between the seal and the tank shell. Excessive gaps will result in higher emissions and will need to be repaired.

Roof fittings: gasketing and slotted guidepoles

There are numerous fittings that are attached to or pass through the floating roof. These allow for sampling, inspection and maintenance hatches and

for support and positioning columns. When fittings require an opening in the floating roof, they become a potential source for evaporative emissions.

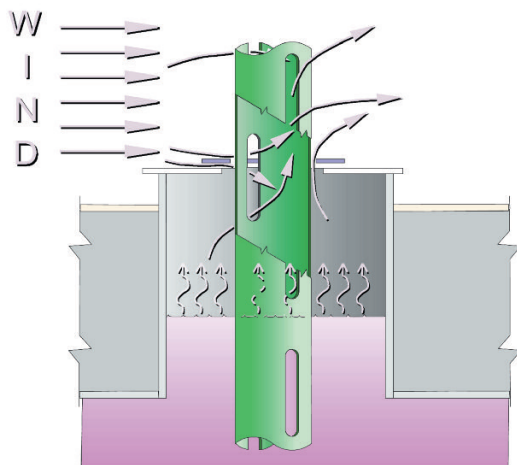
There are two general types of fittings. Hatches allow access to the liquid below the deck for sampling of the liquid and for measuring level. Larger hatches allow access for maintenance personnel. Columns and guidepoles provide support for a fixed roof on internal floating roof tanks and prevent rotation of the floating roof as it moves up and down. In some cases, the columns may also be used for gauging and sampling.

To minimize evaporative losses past hatches, a gasket can be placed around the hatch rim to provide a seal, and the hatch cover can be latched or bolted shut when not in use. For columns and poles, the annular opening between the pole and the floating roof needs to be sealed to prevent evaporative emissions. This can be done with a fabric and rubber wiper arrangement that restricts vapour passage and wipes liquid hydrocarbon off the pole as the roof is lowered. These seals and wiper systems are available from many tank vendors.

Guidepoles come in two types: slotted and un-slotted. Unslotted guidepoles have openings allowing fluid to pass only near the bottom of the pole. There is concern that liquid samples taken through these poles are not representative of the entire tank contents. For this reason, API recommends the use of a 'slotted' guidepole for proper sampling and gauging.

While the slotted guidepole design has advantages for sampling and gauging, it provides additional pathways for evaporative emissions.

Figure 4 Air flow across a slotted guidepole promotes evaporation



In a slotted guidepole, there are holes or 'slots' along the entire pipe which allows liquid to freely flow in and out. While the slotted guidepole design has advantages for sampling and gauging, it provides additional pathways for evaporative emissions; air from above the roof can enter and leave the region below the deck through the openings (see Figure 4).

Figure 5 A sleeve placed around a slotted guidepole eliminates air flow through the slots

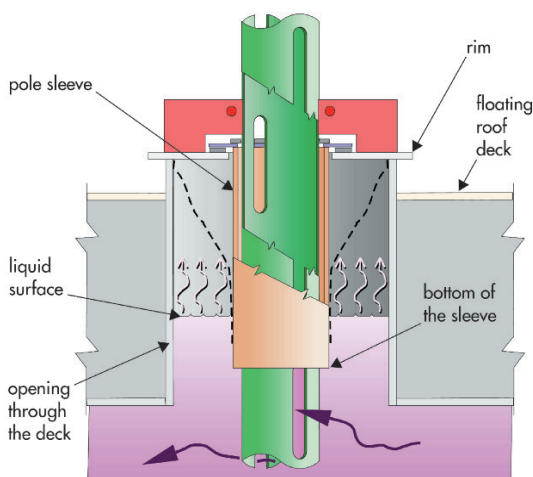


Figure 5 provides an example of a sleeve placed around the slotted guidepole (the dashed lines indicate an alternative location for attachment of the pole sleeve).

In external floating roof tanks, an uncontrolled slotted guidepole can be a significant source of emissions for lighter hydrocarbons. For this reason, it is recommended that consideration be given to placing a sleeve around the slotted guidepole in the region where it passes through the floating roof (see Figure 5). The sleeve should cover all the holes in the guidepole from just above the deck to below the liquid surface.

Gasketing and wipers should be installed to close the annular opening to prevent evaporation and minimize liquid on the pole as the floating roof is lowered. In some cases, the cost of installing the sleeve can be completely offset by the value of the reduced product emissions.

Roof landings

Standard operation of floating roof tanks assumes that there is continuous contact of the floating roof with the liquid below the floating roof.

As material is removed from the tank and the floating roof lowered, the floating roof reaches a level where it becomes supported on roof or deck legs which prevent it from moving any lower. This prevents damage to equipment inside the lower part of the tank, or to deck fittings penetrating below the floating roof. Once the floating roof reaches this level, further withdrawal of liquid causes atmospheric vents to open automatically to avoid excessive vacuum inside the space below the floating roof. At this point, the vapour space under the floating roof is freely vented to the environment above the floating roof, allowing a significant increase in hydrocarbon emissions.

While the floating roof is on its legs and the vacuum breaker vents are open, any liquid that remains in the tank can evaporate, as can any material clinging to the tank walls and poles. In addition, emissions will occur as the tank is refilled causing the vapour below the floating roof to be expelled through the open vents until the floating roof is refloated by the rising liquid.

The quantity of hydrocarbon emissions due to a roof landing depends primarily on the elapsed time of each operation, the quantity of material that remains in the tank while the roof is landed on its deck legs and the vapour pressure of the liquid. In addition, if the tank is drained, the degree of saturation of the remaining gas under the roof has a significant impact. The degree of saturation depends on the design of the tank bottom and how completely the remaining liquid is drained. 'Drain dry' tanks will have lower emissions than tanks with a liquid heel because, in addition to the liquid on the walls and poles that evaporates, the material remaining in the heel will evaporate and be emitted as long as the roof remains landed on its legs.

The primary control to reduce these emissions is to avoid all unnecessary roof landings. If roof landings are necessary to prepare the tank for repair or to change the liquid that is stored, the liquid should be drained as quickly as possible and as completely as possible. Minimizing the elapsed time that the roof remains landed on the deck legs with hydrocarbon liquid present below it will reduce the standing losses. In all cases, vapours will be expelled as the tank is re-filled; collection of these vapours is difficult as there are multiple vents, and access onto the floating roof is not always possible.

Details of the potential loss mechanisms were explored, and methodology for estimating emissions from landing roofs developed, by the American Petroleum Institute (API, 2005).

Cleaning operations

Cleaning and maintenance operations on storage tanks are typically unique to the site, tank and specific event. Many steps are usually involved and not all may occur during a specific cleaning or maintenance event. The steps in preparing a tank for cleaning or maintenance most often include emptying of the hydrocarbon liquid from the tank, removing any of the remaining liquid as best as is possible, purging the tank of hydrocarbon vapours,

removing the sludge from the tank floor and tank wall, cleaning the floor and walls and then, finally, refilling the tank with hydrocarbon. There are alternative procedures available for each step, and the ability to reduce emissions during cleaning and maintenance will be site- and tank-specific. Details of the hydrocarbon loss mechanisms have been explored, and estimating methodology for tank cleaning operations developed, by the American Petroleum Institute (API, 2007).

Initially, liquid is removed from the tank as thoroughly as possible, first through the normal withdrawal procedures, after which any remaining liquid may be collected using vacuum hoses. As liquid is being removed, there are essentially no air emissions from the tank because, for all tank types, the flow of air will be *into* the tank. It is important to remove as much liquid as possible, because any liquid remaining after this step will likely evaporate when the tank is opened.

After all of the liquid is removed, the remaining vapours in the tank are purged. Several purges are normally required to ensure that all hydrocarbon vapours are removed from the tank. In some locations, the first tank volume (sometimes several tank volumes) of this vapour must be collected and treated because of the potentially high hydrocarbon content. Suggested vapour recovery and destruction processes for treating these vapours are discussed in the section on *Product loading* (overleaf).

Removal and collection of sludge may release hydrocarbon vapours. Depending on the specific operation, it may not be possible to collect vapours for treatment during this operation. Operations for cleaning of the tank walls and removal of sludge from the tank floor are usually site-specific and depend on the contractor and methods used. Additional hydrocarbons may be released depending on the procedures and chemicals used. When the tank is returned to service, the normal filling losses occur.



Good practices for control of storage tank emissions

- Inspect roof fitting gaskets and seals and rim seals.
- For external floating roof tanks, replace a vapour mounted primary rim seal with a mechanical shoe seal.
- Install a secondary rim seal on external floating roof tanks.
- Gasket and latch or bolt all roof hatches on external floating roof tanks.
- Install a sleeve around the slotted guidepole in an external floating roof tank.
- Avoid causing a floating roof to land on its legs when withdrawing liquid.
- Drain-dry a tank prior to opening to the environment for cleaning.

Product loading

When hydrocarbons are loaded into rail cars, tank trucks, barges or vessels some of the material loaded evaporates into the vapour space in the compartment. The vapours are then expelled from the compartment as they are displaced by the added liquid. This is similar to the emissions mechanism for fixed roof tank filling losses.

Hydrocarbon emissions during loading are usually from two sources. Initial emissions are predominantly due to vapours from the previous cargo transported (unless the compartment was cleaned). Once these existing vapours are displaced, emissions become predominantly vapours evaporated from the new liquid being loaded.

Loading emissions can be a large source of site hydrocarbon emissions depending on the amount of material loaded, the vapour pressure of the material and the application of any vapour emissions control. Because of the magnitude of loading emissions, some type of vapour control is usually recommended for the higher vapour pressure products such as gasoline. Vapour controls are also typically required on benzene and other toxic liquid loading operations.

The choice of control technology will depend on the quantity and volatility of the material being loaded, the value of any recovered and condensed vapours, the desired emission reduction, local support for the technology, and costs. The costs include both capital and operating costs, and can be significant. As vapour controls on loading are rarely cost-effective based on recovery of the hydrocarbon liquid, they are most often applied due to a regulatory directive. In these cases, the choice of technology must meet the regulatory requirement.

Most vapour control technologies are supplied as package units by vendors who specialize in these types of units. In most cases a complete system is purchased from a vendor who will guarantee the level of performance and provide ongoing operations support.

The typical methods used to control loading emissions are listed in Table 7. A significant reduction in vapour generation is possible by decreasing the turbulence created when liquid is introduced to the compartment. This can be done

Table 7 Controls to reduce product loading emissions

Emission control	Relative cost
Use submerged or bottom loading	Low
Install a vapour balance system	High
Apply vapour recovery	Very high
Apply vapour destruction	Very high

by using bottom or submerged loading rather than splash loading. Vapours can be collected using vapour balancing where the displaced vapour is returned to the container from where the liquid is being emptied. End-of-pipe controls involve collecting the vapours and sending them to a recovery or destruction process. These end-of-pipe controls are usually quite expensive and are typically applied only if required by regulation or if justified for very high value products.

The major types of controls are discussed in more detail in the following sections. In most cases, where vapour recovery or destruction is applied, it provides high levels of control efficiency, but with high capital and operating costs.

How to quantify missions

The quantity and composition of vapours emitted from loading hydrocarbons will depend on the material previously contained in the compartment, any compartment cleaning before loading, the vapour pressure of the material being loaded, the method of loading and the use of any vapour controls.

There are several ways to estimate emissions from product loading operations. The simplest, and potentially least representative, is to use industry average emission factors for each type of liquid. Improved estimates are possible if more information is known about the vessel, its condition and the type of loading. If specific vapour pressure information on the material being loaded is available, even more representative emission

estimates are possible. These emission estimating options are discussed in US EPA, 1995b.

Splash, bottom and submerged loading

How material is placed into the receiving container makes a significant difference in hydrocarbon vapour generation. Turbulence that tends to increase vapour concentrations should be minimized. If new product is added above the liquid, significant splashing can occur which will increase vapour concentrations and create droplets that can be entrained with the escaping vapour as it is displaced by the liquid. For this reason, splash loading from above the liquid surface is not recommended.

Alternatives to splash loading include submerged and bottom loading. In submerged loading the pipe through which new liquid is loading is placed very near the bottom of the container. This minimizes splashing as the liquid entry point will quickly become submerged in the compartment. In bottom loading, the pipe enters from below the floor of the compartment and is always maintained below the liquid surface.

Vapour balancing

In vapour balancing, hydrocarbon vapours are collected from the compartment where the liquid is being loaded and returned to the tank from which the liquid is being sent. This works because the volume of displaced vapours is almost identical to the volume of liquid removed from the tank. The

technique is used mostly when loading tank trucks from fixed roof tanks. It cannot be applied when loading from floating roof tanks since there is no closed vapour space in the tank to which vapours can be returned.

Vapour balancing sends the displaced hydrocarbon vapours to the tank in place of external air that would normally enter the tank as the level is lowered. This reduces the volume of air that becomes contaminated with hydrocarbon vapours. When refilling the tank, these vapours will be expelled and controls need to be considered if they cannot be sent to another compartment for balancing.

Vapour recovery: adsorption, absorption and refrigeration

Vapour recovery provides control of emissions by collecting the vented material for recycle and reuse. The three types of technologies most often applied are adsorption, absorption and refrigeration. The operating characteristics of these technologies are provided in Table 8. In some cases, combinations of technologies such as absorption followed by adsorption have been applied. These combinations sometimes provide both higher capacity and lower vapour concentrations more cost-effectively.

Adsorption involves capture of vapour by a highly porous solid. Carbon is the most commonly used adsorbent but many proprietary adsorbents are currently offered by vendors, including silica gel, alumina or zeolite based products. Adsorbents with high surface area to volume ratio are desired.

There are two types of adsorption unit, each of which uses a different method to regenerate the adsorbent. One uses vacuum regeneration and one uses thermal regeneration, often with steam. Some small and infrequently operated vapour control units may, more economically, use carbon canisters which are replaced rather than regenerated on site.

A typical adsorption unit that is in continuous operation will consist of two or more adsorbent beds. This allows at least one to be treating vapours while the other is being regenerated. Vapours removed during regeneration are often condensed and recycled to the product tanks.

Control efficiencies for adsorption depend on the vapour flow rate, temperature, operating pressure and adsorbent. In general, adsorption increases with increasing molecular weight of the hydrocarbon and operating pressure, and decreases with increasing temperature. Adsorption units can often provide high control efficiency but at high operating costs. They are mostly applicable to lower flow rates and lower hydrocarbon vapour concentrations.

Table 8 *Characteristics of vapour recovery technologies*

Technology	Secondary impact	Pretreatment requirements	Feed concentration range (ppm)	Approximate control efficiency (%)
Adsorption	Solid waste	Cooling Dehumidification Particulate removal	20–2,000	90–99
Absorption	Solid waste Wastewater	Particulate removal	1,000–20,000	50–95
Refrigeration	Solid waste Wastewater	Dehumidification	5,000+	50–80

Absorption recovery units involve the mass transfer of hydrocarbon from a gas stream into a liquid solvent. In many cases this is just a liquid hydrocarbon of higher molecular weight. The rate of absorption and maximum capacity is determined by the equilibrium concentrations of the liquid and gas phases. Removal efficiency is mostly determined by the solubility of the hydrocarbon in the absorbent and the intimacy of vapour-liquid contact.

Absorption tends to be less efficient than some other techniques and, as previously mentioned, is often used in combination with another technology such as adsorption. Absorption can handle a wide range of vapours and can accommodate larger changes in vapour flow and concentration. However, absorption units cannot usually achieve the same level of removal efficiency as carbon adsorption beds.

In refrigeration, also known as condensation, hydrocarbons are removed from the gas by lowering the gas temperature. Sometimes increased pressure is used in place of lower temperature. There are two types of condensers: surface and direct contact. In surface condensers, coolant flows on one side of a heat exchanger, condensing the hydrocarbons as the gas flows on the other side of the heat exchanger. In shell and tube heat exchangers, the coolant usually flows through the tubes and the gas stream is on the shell side. Contact condensers operate by spraying a cool liquid directly onto the gas stream. A major advantage of vapour recovery by refrigeration is the ability to recover relatively pure hydrocarbon. However, these systems tend to have relatively lower recovery efficiencies and higher operating costs.

Table 9 Advantages and limitations of vapour recovery technologies

Technology	Advantages	Limitations
Adsorption	<ul style="list-style-type: none"> • Very high efficiency • Potential recovery of very high purity stream • No open flame (but exothermic reaction needs monitoring) • Applicable to very low stream concentrations • Applicable to batch operations 	<ul style="list-style-type: none"> • Limited capacity with maximum throughput and concentration allowances • Requires low humidity • Requires low temperatures • Potential to plug or poison adsorbent packed bed • May require prefiltering of gas • Less efficient for light molecular weight species • Swing operation to allow regeneration in continuous operation
Absorption	<ul style="list-style-type: none"> • Typical process-like operation • Potential recovery of high purity stream • Low pressure drop • Lower energy consumption • No open flame 	<ul style="list-style-type: none"> • Not efficient for low concentrations • Not efficient for low gas volumes • Recovered product may need to be separated from lean oil • Lower capture efficiencies
Refrigeration	<ul style="list-style-type: none"> • Direct recovery of pure product possible • No open flame • Applicable to high concentration streams 	<ul style="list-style-type: none"> • Potential high energy costs • Lower collection efficiencies • Not efficient for low flash temperature streams

Condensers are often used in combination with other control techniques. They can be located upstream of absorbers, carbon beds or oxidizers to recover some product and to reduce the hydrocarbon being treated by these other units.

The advantages and limitations of these vapour recovery technologies are summarized in Table 9.

Vapour destruction: flares, thermal oxidizers and catalytic oxidizers

Vapour destruction provides control of emissions by combustion of the hydrocarbon to form carbon dioxide and water vapour. The three types of technologies most often applied are flares, thermal oxidizers and catalytic oxidizers. The operating characteristics of these are provided in Table 10. While vapour destruction reduces emissions of hydrocarbon, because it is a combustion process, it can increase emissions of NO_x and, if sulphur is present, SO_x . Destruction efficiency is controlled by residence time, combustion temperature and oxygen availability.

In some cases, vapours can also be controlled by routing the gas to a boiler, heater or furnace. This allows recovery of the heating value of the material. Applicability will depend on location within the plant and on compatibility of the vapours as a supplemental fuel.

The least expensive destruction technology is often flaring. Flares can be elevated and open or enclosed at ground level. Open, elevated flares

have a flame located at the top of a stack and use specially designed burners. They are most often used for controlling emissions from plant upsets. Steam assist is often used to provide increased turbulence and mixing with air which increases destruction efficiency.

Ground level flares are enclosed and contained in an insulated shell. The shell provides reduced noise and visibility. Enclosed ground level flares are used for continuous streams and provide more stable operating conditions than do elevated flares.

Thermal oxidizers or incinerators are controlled combustors. They include a combustion chamber that is designed to completely contain the flame at maximum firing rate to ensure sufficient residence time at flame temperatures to maximize destruction. Operating parameters that affect emissions control include the supplemental fuel firing rate, residence time, gas mixing and exit temperature. Good gas mixing with supplemental combustion air is essential for high destruction efficiencies.

There are three different designs for thermal oxidizers depending on the type of heat recovery employed: direct flame, recuperative and regenerative. Direct flame units do not include any heat recovery from the combustion process. Recuperative designs include heat exchangers to preheat the feed gas with the flue gases from combustion. Regenerative designs transfer the heat first to an intermediate material (usually ceramic beds) and then to the feed gas. The regenerative designs are usually more thermally efficient due to better heat transfer.

Table 10 *Characteristics of vapour destruction technologies*

Technology	Secondary impact	Pretreatment requirements	Feed concentration range (ppm)	Approximate control efficiency (%)
Flares	CO_2 , SO_x , NO_x	Liquid removal		98 +
Thermal oxidizer	CO_2 , SO_x , NO_x	Preheating	20 – 20,000	95 – 99
Catalytic oxidizer	CO_2 , SO_x , solid waste	Preheating Particulate removal	50 – 10,000	90 – 98

In catalytic oxidizers, the combustion occurs at a much lower temperature in the presence of a catalyst that promotes complete combustion. Destruction efficiency depends on the hydrocarbon concentration, operating temperature, residence time, catalyst activity and oxygen availability. As residence time and temperature increases, destruction efficiency increases. Since these units operate at lower temperatures, there is much less formation of thermal NO_x . However, catalytic oxidizers are susceptible to plugging and poisoning by metals in the hydrocarbon vapour. As the catalyst activity decreases, it must be replaced or regenerated.

The advantages and limitations of vapour destruction technologies are summarized in Table 11.

The selection of a specific vapour control technology will depend on the regulatory requirements and the capital and operating costs. If

several technologies will meet the regulatory requirements and have similar costs, factors such as the range of applicable flow rates, vapour concentrations and stream consistency become important in selection. Options should be discussed with local vendors supplying package units as they will typically provide ongoing operations support and a performance guarantee.

Good practices for control of loading emissions

- Apply bottom or submerged loading of material to reduce vapour generation.
- Consider vapour balancing opportunities.
- Consider vapour recovery opportunities.
- Work with local vendors supplying package vapour control units.
- Have vendor guarantee recovery efficiency.

Table 11 Advantages and limitations of vapour destruction technologies

Technology	Advantages	Limitations
Flares	<ul style="list-style-type: none"> • Low cost • Treats wide range of flows and concentrations 	<ul style="list-style-type: none"> • No product recovery • No energy recovery • Routine flaring to be minimized • Emissions of products of combustion (CO_2, SO_x, NO_x) • Limits on placement due to noise and safety
Thermal oxidation	<ul style="list-style-type: none"> • High control efficiency • Treats a wide range of stream concentrations • Possible energy recovery 	<ul style="list-style-type: none"> • Emissions of products of combustion (CO_2, SO_x, NO_x)
Catalytic oxidation	<ul style="list-style-type: none"> • High control efficiency • Possible energy recovery • Lower energy consumption than thermal oxidation • Lower NO_x formation 	<ul style="list-style-type: none"> • No product recovery • Catalyst plugging and poisoning • High pressure drop

Wastewater collection and treatment

Hydrocarbon emissions from the wastewater collection and treatment system occur as a result of evaporation of hydrocarbon from the water where there is water-air contact and release of the vapour to the environment where the system is open to the outside. In most plants, many parts of the collection and treatment system are typically open to the environment.

The wastewater collection system includes components such as drains, manholes, junction boxes and sewers. Where each is open to the environment there may be emissions of hydrocarbon. The treatment system in each plant is unique but will typically include a primary oil/water separator, holding and equalization tanks or basins and possibly flotation and biological treatment units. Where each of these treatment units is open to the environment, and there is air-water contact, emissions of hydrocarbon can occur.

The emission control strategies for wastewater systems are to minimize wastewater generation, to reduce hydrocarbon concentrations entering the system and to reduce the area of air/water interface.

Wastewater typically contains a variety of hydrocarbon compounds with widely varying concentrations. The compounds present and concentrations are usually site specific. The best way to minimize hydrocarbon emissions from the wastewater collection and treatment system is to reduce the quantity of hydrocarbon that enters the system.

Sometimes it is possible to better manage wastewater by segregation or recycle. Drains and sumps should not be used for routine disposal of process fluids or for discharge from sampling lines. Drains and pads can be raised to reduce storm water entry. Having separate process and storm water systems will reduce contamination. Optimizing strippers to lower hydrocarbon concentration will reduce the quantity entering the collection and treatment system. Once wastewater enters the treatment units, control usually involves covering them, and in some cases, controls on the collected and vented vapours.

Water can become contaminated with hydrocarbons intentionally, through direct contact, or accidentally, through indirect contact. Intentional sources include units that use water for washing

Table 12 Controls to reduce wastewater collection and treatment emissions

Emission control	Relative cost
Decrease wastewater volume	Low
Decrease wastewater hydrocarbon concentration	Low
Leak detection programme for heat exchangers	Low
Optimize stripper operation	Medium
Install sewer system emissions controls	Medium
Segregated process and storm water systems	High
Reduce air/water interface	High
Cover separation and treatment units	High
Apply vapour destruction	Very high
Apply vapour recovery	Very high

such as desalters and sour water strippers. Water may also be formed as a byproduct of reaction or may be mixed with process fluids in tank draw-off, storm water run-off and steam eductor condensate.

Accidental or indirect sources are those that do not normally come into contact with hydrocarbon as part of the process. These sources include process fluid leaks from cooling heat exchangers, condensers and pumps. In addition, pump seal water may be collected in local drains that flow into the wastewater sewer system. A heat exchanger leak detection programme is the most effective approach to minimizing hydrocarbon contamination of cooling water. Individual exchangers with leaks can be identified and plans can be made for tube repair.

Once contaminated water enters the treatment units, emissions control opportunities are limited to reducing the air-water contact area and collecting vapours for treatment. Although not justified by cost, some separator and treatment units can be covered to reduce wind driven evaporation. Options to reduce hydrocarbon emissions from wastewater collection and treatment and their relative costs are provided in Table 12.

How to quantify emissions

There are two general ways to estimate hydrocarbon emissions from wastewater collection and treatment. One involves the use of industry average emission factors. While this method is simple, and all that is usually needed is the unit flow rate, it is not likely to produce representative estimates and the predicted quantities will tend to significantly exceed the actual unit emission rates in a well-run plant.

A more representative method for estimating emissions involves the use of computer models; however, this is complex and requires a significant amount of design and operating data. Also, these models calculate individual chemical compound

emissions so knowledge of all the hydrocarbon compounds in the wastewater is required to accurately estimate total hydrocarbon emissions. However, as stated, these models will provide much more representative estimates of emissions. The US EPA has developed a computer model for estimating hydrocarbon emissions from the wastewater system (US EPA, 2004).

Source reduction

As previously mentioned, the best way to minimize emissions from the wastewater collection and treatment system is to reduce the quantity of hydrocarbon that enters the system. Waste minimization includes flow and/or concentration reduction as well as recycling. Sometimes, source reduction can be achieved through process or equipment modification, stream segregation, or improved work practices.

Guidelines for reducing the quantity and hydrocarbon content of wastewater can be found in IPIECA, 2010.

Sewers, drains, junction boxes and lift stations

Most wastewater from process areas enters the collection system through drains which are connected to the sewer system. There can be significant evaporation from the system if the drain is not sealed and vapours are allowed to escape. A water seal, often called a p-trap, can be used to effectively eliminate these emissions. This reduces the vaporization of hydrocarbon in the wastewater as it enters the drain and also prevents hydrocarbon vapours already in the sewer system from escaping. In open sewers, air passing through can be a promoter of increased emissions as wind passing over the drain can create a vacuum-like effect.

Inspection and cleaning of sewer lines is accomplished by the presence of manholes which

allow access for maintenance personnel and equipment. A sewer line may have many of these placed along its length. If the manhole is not properly sealed, hydrocarbon vapours from the sewer system can be released. As with open drains, air passing through due to an ineffective seal or holes in the manhole can promote increased emissions as wind passes over the manhole and creates a vacuum-like effect. An effective control can be obtained by completely sealing all openings in the manhole so that vapour release and air passage is prevented.

Junction boxes are used to collect the flow from several sewer lines. Where these are open to the environment, hydrocarbon vapour emission can occur. Turbulence in the junction box can significantly increase the potential for hydrocarbon emissions. The junction box should be designed so that wastewater streams enter below the liquid surface to minimize splashing and turbulence. Also, to reduce overall evaporation, residence time of the wastewater in the junction box should be minimized.

The final part of the wastewater collection system is usually a lift station. This uses a pump to physically raise the water so that it has sufficient pressure head to flow to the treatment system. In some cases, there is an open top on the lift station. Typically, there is a periodic operation of the pump. As water enters the lift station sump and the water level increases, the pump will begin to operate when the water reaches a specified level and will cease operation when the water level has been reduced to a lower, specified level.

In lift stations, there are two mechanisms that promote emissions. At lower water levels, hydrocarbon emissions are enhanced by splashing and turbulence as new wastewater enters the lift station. As the water rises in the lift station, it pushes existing hydrocarbon-contaminated vapours out of the top of the lift station. As with the other collection system units,

emissions can be essentially eliminated by closing the lift station so that vapour cannot flow into the environment.

Controlling the hydrocarbon emissions from the wastewater collection system by enclosing it will normally result in the wastewater having a higher concentration of hydrocarbons when it enters the treatment units. Emissions prevention during collection can result in almost the same quantity of hydrocarbon emissions being released during treatment. Therefore, for the system to be considered effective, at some point the hydrocarbons need to be recovered or destroyed.

If some control of hydrocarbon vapours occurred in the collection system there could be a reduction in the emissions from the treatment system. This could be achieved using carbon canisters on collection system vents, which would need to be periodically replaced.

Primary separators, IAF/DAF, biological treatment and treatment tanks

Wastewater treatment systems generally consist of primary, secondary and occasionally, tertiary treatment units. In the treatment system, hydrocarbon species are removed from the wastewater via three pathways. They can biodegrade into other species and, eventually, into carbon dioxide and water; they can adsorb into the sludge and be removed; or they can be released as vapours into the air. The specific design and operation of each unit will determine the relative amounts for each pathway.

Primary treatment separates free oil and most solids from the wastewater. In the primary oil/water separator, oil and solids are separated from the wastewater by gravity. As the contaminated wastewater flows across the separator, oil floats to the top of the water phase where it can be removed for reprocessing. Heavier

solids sink to the bottom of the separator and are removed for disposal.

Hydrocarbon emissions from oil/water separators depend on a number of factors including the concentration of the specific hydrocarbon, the hydrocarbon volatility, wastewater and air temperatures, and wind speed. Though not cost-effective, covering the unit with either a fixed or floating roof results in the greatest emission reduction since the ambient air-water interface is eliminated. Fixed roofs may require inert gas blanketing to avoid an explosion hazard. The emissions control effectiveness of the roof is largely dependent on the sealing between the walls of the separator and the roof.

After the primary separator, a dissolved air flotation (DAF) or induced air flotation (IAF) unit is used for further oil/water separation. In these units, the water mixture is subjected to physical and chemical procedures that promote the aggregation of suspended solids into particles large enough to be removed. In the DAF unit, a recycle stream is pressurized with air which, when returning to the DAF unit, creates small air bubbles that promote the flotation of oil and some solids. In an IAF unit, air is induced into the fluid by a rotating mechanism and then rises, collecting oil and solids. Any oil collected on the surface of the flotation unit has the potential to volatilize. Covering these units with a fixed roof can allow any volatilized vapours to be collected and prevented from being released to the atmosphere. Proper precautions to mitigate or prevent explosion hazards on these covered units are important aspects of unit design.

Equalization basins are used to reduce fluctuations in wastewater flow rate and concentration to subsequent treatment units. They may be located before or after the primary treatment units. As wastewater flows through the basin, hydrocarbons diffuse through the water to the liquid surface and evaporate. In some cases, aerators are used in equalization basins to add oxygen for subsequent

treatment. This aeration has the potential to enhance evaporation due to the additional turbulence and increased surface areas of the liquid coming into direct air contact.

Secondary treatment units remove dissolved hydrocarbons remaining in the wastewater. Biological treatment is normally conducted in aerated basins. These units use diffused or mechanical aeration to provide oxygen for the biological processes. In these units organic material is converted into cell tissue, water and carbon dioxide.

Some treating operations can be conducted in fixed or floating roof tanks. This will usually provide significant emission reduction compared to open-top systems. By covering the surface of the wastewater, evaporation of the hydrocarbons is reduced. If there is sufficient hydrocarbon to cover the liquid surface, emissions from fixed roof tanks can be significant and a floating roof tank may need to be considered. The section on *Storage tanks* (page 18) discusses emission controls.

As with other treatment units, tank emission controls often result in the hydrocarbon continuing to remain in the water until a later opportunity arises for it to evaporate. Actual emission reduction is only achieved if the hydrocarbon is recovered or destroyed.

Good practices for control of air emissions from wastewater collection and treatment

- Reduce concentration of hydrocarbons in wastewater.
- Reduce volume of wastewater that needs to be treated.
- Consider whether seals can be applied to drains, manholes and junction boxes.
- Consider whether the air/water interfaces on wastewater treatment units can be covered.

Process vents

Atmospheric process vents are generally pipes connected to vessels that emit process gases directly into the environment. They may be located on reactor vessels or other process fluid receiving vessels that require removal of material after reaction or separation. In many cases the vents will be open directly to the atmosphere. Alternatively, there may be a pressure relief valve that allows only occasional release of the process fluid to the environment. The best control for these process vent emissions is to eliminate the need for discharge by altering the process operation or recycling the material. If this cannot be done, vapour controls such as recovery or destruction can be considered for application to the vent stream.

The first step in controlling process vent emissions is to determine whether there are economic alternatives to venting such as direct recycle or temporary storage and reuse or recovery. Possibilities will be specific to the process unit. Recovery options such as refrigeration, absorption and adsorption are discussed in the section on *Product loading*.

In some cases, vapour destruction as a control for process vent emissions may be the best option. Types of vapour destruction controls may include flares, incinerators or other oxidation type units discussed in the section on *Product loading*. Generation of combustion emissions from all of these destruction-based controls should be accounted for and considered in the technical evaluation.

Good practices for controlling process vent emissions

- Evaluate options for recycle and reuse of discharged material.
- Consider vapour recovery options such as condensation, adsorption and absorption.
- Consider vapour destruction options such as flares, incineration and catalytic oxidation.

Flares

The refinery flare system exists to prevent a major accident should a process upset or other condition require the shut-down of a process unit releasing flammable gases. As such the flare system is an essential safety device.

Intermittent releases from vents and pressurised relief valves may be directed to flare as a preferred alternative to venting to atmosphere.

Routine flaring of waste gases is deprecated for both overall efficiency and environmental reasons. A refinery flare minimisation plan should be developed as part of the overall environmental management system.

Although flares are external combustion sources with limited control of the combustion process, a well operated flare will generally have a combustion efficiency of 99.5%.

There are many designs of flare used in refineries. The flare tip design is important to assure flame stability in different meteorological conditions, low noise, good combustion performance, etc., which may be aided by steam injection for minimization of visible smoke.

Source reduction

The most effective way to reduce flare emissions is to minimize the amount of material sent to the flare.

The sources are:

- necessary fuel for the flare pilot flame to ensure ignition in the event of emergency;
- emergency venting;
- vented gases from process upsets, start-up and shut-down of operations;
- surplus gases from production processes; and
- vented gases from normal operations, pressure relief valve operation, etc.

Improved operation of processes can lead to a reduction in the number of emergency flaring episodes, thus reducing the quantity of gas sent to the flaring system. In addition, the installation of a flare gas recovery system to recycle the hydrocarbons back into the process system and/or refinery fuel gas system is an option that is widely applicable in refineries where there is a surplus of gas from processes.

Gas recovery

A flare gas recovery system comprises pipe headers to collect the gases, condensers to remove any liquids, and compressor(s) to recycle the gas back to the process or into the refinery fuel gas system.

The cost-effectiveness of flare gas recovery may vary widely between sites depending upon the nature and distribution of the sources of material going to flare. It will be less favourable for numerous distributed sources and for gases needing pre-treatment for further use.

Sources and control of combustion emissions

Combustion processes can be divided into two groups. The first group involves the burning of fuels to use the heat of combustion to raise the temperature of a fluid other than the fuel (e.g. in various pieces of process equipment including furnaces, boilers and heaters). The second group involves combustion of part of the material being processed to provide heat to conduct the reaction (e.g. catalytic crackers, catalytic reformers, steam/methane reformers and sulphur plants). Both of these groups can result in the generation of sulphur oxides, nitrogen oxides and particulate matter depending on the fuel and fuel components, unit design and operation.

Boilers, heaters and furnaces

Boilers, furnaces and heaters are utilized to raise the temperature of water, other heat transfer fluid or a process stream. This is accomplished by burning a fuel and using the heat of combustion to raise the temperature. The heat is transferred to the water, heat transfer fluid or process fluid by radiation from the flame and convection and conduction from the combustion gases. Reduction in fuel use typically results in a proportional reduction in most emissions. Therefore, energy conservation efforts

can often have direct impacts on reducing emissions. An exception to this is combustion air preheating which raises the flame temperature and can sometimes result in increased NO_x formation.

Particulate matter (PM) can take more than one form. 'Primary particulates' usually refers to solid materials such as soot or catalyst. The soot is often formed from incomplete combustion of the fuel or from intermediate combustion products. Typically, gaseous fuels have lower amounts of primary particulate emissions than liquid fuels which, in turn, have lower primary particulate emissions than solid fuels. 'Secondary particulates' usually refers to precursors of sulphates and nitrates, and also to aerosols that can be condensed from the flue gas at specific temperatures. The quantity of aerosol emitted is defined by the condensing temperature of the flue gas sampling system. As with primary particulates, gaseous fuels typically have lower amounts of secondary particulate emissions than liquid fuels which, typically, have lower secondary particulate emissions than solid fuels. Carbon deposited on (and subsequently burned off from) a catalyst, such as in FCC units, is considered a solid fuel.

Sulphur oxides are created in combustion processes when sulphur in the fuel is burned. The amount of SO_x emitted is directly proportional to the concentration of sulphur in the fuel. Typically, gaseous fuels have lower amounts of sulphur than liquid fuels which have lower sulphur than solid fuels. Some gaseous fuels that are generated within a refinery process (e.g. refinery fuel gas) can have higher sulphur contents and may require pre-treatment to lower the amount of sulphur prior to use.

There are two combustion mechanisms that produce nitrogen oxides. Nitrogen oxides are created when nitrogen and oxygen in the air combine at high temperatures. This formation mechanism produces 'thermal NO_x '. For fuels with significant elemental nitrogen content (e.g. liquid fuels like oil, and solid fuels like coal or coke) this fuel-bound nitrogen can



be a large contributor to NO_x emissions. This formation mechanism produces 'fuel NO_x '.

How to quantify emissions

Emissions of NO_x and PM are typically estimated using industry average emission factors from AP-42 (US EPA, 1995b) and CONCAWE (CONCAWE, 2009). There are different factors for different unit types, fuels and sometimes operations. When estimating NO_x emissions, adjustments can be made for a myriad of operating parameters such as fuel hydrogen content and ambient humidity. PM factors are provided for both primary PM and secondary PM for most units. Although average emission factors are fully accepted, stack testing provides a more representative method to assess PM and NO_x emissions, but at much higher cost.

Emissions of SO_x are usually based on assuming all the sulphur in the fuel is combusted and forms the oxide. Thus, a direct material balance assessment on the quantity of sulphur in the fuel burned is the standard procedure for calculating SO_x emissions.

PM (particulate matter) control

PM, or dust, generally refers to any solid, aerosols and liquid droplets. The technologies available for PM control include mechanical collectors, bag houses and filters, electrostatic precipitators and wet scrubbers. The choice of control will depend on the size and weight distributions of the particles to be removed and the emission limit. In some locations, 'total' PM is no longer regulated, as the focus of control is now on particulate matter less than 10 microns in diameter. Most of these control technologies require significant plot space, which may be a limitation in retrofit applications.

PM control efficiency is based on the mass of particulates collected rather than the number of particles collected. Most PM control devices have high efficiencies over specific particle size ranges. The control device should be selected based on the

particle size distribution containing the greatest mass percentage of PM. In that way, the greatest PM mass reduction can be achieved.

Mechanical collectors control particulates by using gravity or inertial forces to separate the particle from the gas stream. These include cyclones, other inertial collectors and settlers. In cyclones, particulates follow the gas stream along the circumference of the cyclone and move toward the exterior wall due to inertial forces. They are disengaged from the gas at the bottom of the cyclone where the gas quickly changes direction to exit the cyclone. Multi-stage cyclones can often achieve high particulate removal efficiencies. Smaller-sized cyclones can also provide greater removal efficiencies, but pressure drops are higher.

In inertial collectors, separation is based on the difference between the densities of the particles and the gas. The gas is redirected through quick turns which, although easy for the gas, is more difficult for the particles because of their higher inertia. Units may include baffles and other obstruction-like systems where the particulates are intercepted as the gas flows by; the particulates then settle and are removed. Sometimes these units are called 'impingement separators'. These devices are generally not very efficient except for the removal of larger-sized particulates. Sometimes, an inertial separator can be used as a preliminary 'cleaning' unit for larger particles prior to removal of smaller particle 'fines' in a downstream unit.

The cyclone is a special type of inertial separator since it combines promoting particulate movement down and to the sides of the cyclone in addition to a quick change in gas direction. As described above, cyclones are often used in multiple stages to achieve higher PM removal efficiencies.

In settling chambers, the gas velocity is lowered and the particulates fall out of the gas due to gravity. The advantages of settling chambers

Table 13 Controls to reduce PM emissions

Emission control	Relative cost
Substitution liquid fuel for imported natural gas	Medium
Cyclones, settling chambers and inertial collectors	Medium
Fabric filters	High
Wet gas scrubbers	High
Electrostatic precipitators	

include low maintenance and low pressure drop. Although these units are not efficient for small-sized particulates, they can be used for preliminary ‘cleaning’ prior to removal of ‘fines’. The chamber is designed such that the flue gas is at a sufficiently low velocity for a large fraction of the particulates to settle to the bottom region of the chamber where they enter hoppers and are removed. Gas velocity must be set to minimize re-entrainment of the particulates once they are collected. In some cases, improved performance can be obtained by including a number of flat plates in the chamber to create shorter settling distances.

Bag houses contain fabric filters that collect particulates as the gas passes through the fabric. They usually provide very high collection efficiency but are unsuitable for high temperature combustion streams without additional cooling. Therefore, bag houses usually require cooling of the combustion flue gas. Also, the pressure drop can increase over time as particulates are collected; therefore, the bags are usually cleaned by agitation and/or reverse flow using clean gas. Collection efficiency may be lower after the bags are cleaned since some build-up of particulate on the fabric is required to enhance the removal of PM.

In wet gas scrubbers (WGSs), water is sprayed into the gas stream and the water droplets intercept and collect the particulates. Scrubbers can handle high temperature combustion streams but they produce liquid waste containing particulates that may need to be treated.

Scrubbers can also be used to reduce SO_x by selecting an appropriate liquid absorbent. In cases where emissions of both PM and SO_x need to be reduced, use of a WGS should be considered. Scrubber technology is generally sold by vendors who often offer ‘turnkey’ services.

In electrostatic precipitators (ESPs), the particles are charged and then pass through a chamber with electrodes that attract the particulates due to the difference in charge. The collecting electrodes are usually plates that are occasionally cleaned by ‘rapping’ which causes the particulates to fall to the bottom of the chamber and into a hopper for removal. ESPs are generally sold by vendors as package units specifically designed for individual site application.

Substitution of liquid fuel for imported natural gas is an option for emissions control for all three main pollutants.

Note that the pressure drop across combustion systems is a limiting factor for the use of secondary measures.

SO_x control

The emissions of SO_x from furnaces, boilers, heaters and other external combustion units can be controlled in three ways. Two involve reducing the quantity of sulphur in the fuel to the unit. This may be done by treating the fuel to reduce sulphur or by substituting a lower sulphur fuel such as a gas

for a liquid. The third way is to apply end-of-pipe controls such as scrubbers.

Since any sulphur in the fuel will, when the fuel is burned, result in formation of SO_2 , reduction of sulphur in the fuel will result in a proportional reduction in SO_2 emissions. If currently using fuel oil, switching to gas (which usually has much lower sulphur content) will typically reduce SO_2 emissions. In some cases, sulphur may need to be removed from refinery fuel gas if it is high in sulphur content.

Treating liquid fuels (usually with hydrogen in a hydrodesulphurization process) to remove sulphur compounds is another way to decrease the formation of SO_2 . However, costs can be high depending on the required level of sulphur removal and this is not usually seen as a technique which is used specifically to prepare internal refinery fuels but to control the refinery product slate. Refinery fuels may benefit as a consequence.

Scrubbers provide for gas contact with an absorbing liquid (usually an alkali water mix) which removes the SO_2 . There are several alternative scrubbing technologies. These are generally characterized as either once-through or regenerative systems, and either wet or dry processes. The once-through systems use an absorbent that is not recyclable. Regenerative systems recycle the spent absorbent after sulphur compound removal to produce sulphur or sulphuric acid. As mentioned above, wet scrubber systems can also be used to simultaneously reduce PM emissions.

The most commonly applied wet systems use lime or limestone. Although these systems are lower in cost and have the largest experience base, they require treatment and disposal of waste sludge. In many wet systems, the SO_2 is converted into a sulphate. The liquid is collected and treated before recycle. After time, fresh liquid is added and a portion of the contaminated liquid is removed as a waste stream. Usually, a significant amount of

Table 14 Controls to reduce SO_x emissions

Emission control	Relative cost
Fuel substitution	Medium
Scrubbers	High

equipment is required for treating the spent slurry from the wet systems, including clarifiers, filters, centrifuges and settling ponds.

Scrubbers require significant plot space, which may be a limitation in retrofit applications. Another concern in wet scrubbers is scale formation and plugging at higher pH. Slightly basic conditions are usually optimal for SO_2 removal. However, these are the same conditions that will enhance scale formation and plugging.

Some newer WGS applications have used seawater. This is applicable only to sites near the sea. Water treatment can sometimes result in the release of SO_2 during aeration, decreasing the control efficiency of the system.

There are 'dual-alkali' processes where a sulphate is used to absorb the SO_2 in place of the limestone slurry. The spent slurry is then regenerated using lime. These processes eliminate the scaling problems of the lime and limestone scrubbers by eliminating calcium in the scrubber. However, these two-step systems are more complex and costly to operate since the lime needed for regeneration is generally more expensive than limestone.

In dry scrubbing, a solid sorbent is injected into the flue gas stream. The sorbent particles, which collect sulphur compounds, are collected downstream using conventional PM control methods. These systems reduce the need for much of the water handling, and the waste is a more easily handled solid rather than sludge.

There is much less experience with the dry systems than with wet systems, and they often use lime

rather than limestone. It is believed that much of the SO_2 removal occurs in the particle collection device as the gas contacts the sorbent. For this reason, filters are the preferred PM collection device.

Note that the pressure drop across combustion systems is a limiting factor for the use of secondary measures.

NO_x control

As discussed earlier, there are two types of NO_x : thermal NO_x created in combustion processes when nitrogen and oxygen in the air combine at high temperatures; and fuel NO_x which involves conversion of elemental nitrogen chemically bound to carbon in the fuel. Controls for thermal NO_x involve reducing NO_x formation by altering the combustion process or by end-of-pipe treatment. Controls for fuel NO_x include reducing nitrogen in the fuel used and end-of-pipe treatment.

Thermal NO_x formation is a function of the flame temperature, residence time and the air-to-fuel ratio. Combustion modifications can be implemented that reduce the flame temperature and the time that the flue gases are at the maximum temperature. Usually, operating in the most efficient manner for heat recovery, with high temperatures and longer residence times, tends to promote thermal NO_x formation. Reducing excess air (i.e. excess oxygen) and operating closer to the stoichiometrically required amount of air for complete combustion will reduce NO_x formation. Unit design and control to promote thorough air-fuel mixing for complete combustion becomes critical at near stoichiometric conditions.

There are several methods to reduce flame temperature including staged combustion, flue gas recycle and steam injection. In staged burners, the initial stage operates fuel rich (i.e. oxygen deficient) at high temperature while the second stage, which completes the combustion, operates at a lower temperature resulting in lower overall NO_x formation.

These 'low- NO_x ' burners have varying performance depending on the size of the burner and the fuel.

Newer burner designs alter flame geometry, turbulence and combustion sequencing to reduce thermal NO_x formation. These can include localized gas recirculation and delayed mixing of combustion air. The latter reduces flame temperature since there is lower localized excess air, resulting in reduced NO_x formation. Vendors offer advanced designs that can provide for very low NO_x formation when using gaseous fuels. Several vendors offer 'ultra-Low NO_x ' burners for new units. However, these newer burner types are not always applicable for retrofits in existing units due to space limitations.

Small amounts of flue gas can be returned to the combustion chamber to reduce the flame temperature. In this configuration, oxygen is diluted, resulting in slower combustion and less oxidation of the nitrogen.

For fuel oil fired units, the majority of NO_x formation in low NO_x burners is due to nitrogen bound to the carbon in the fuel. This 'fuel NO_x ' can be addressed by processing the fuel oil to reduce nitrogen content. An alternative is to switch to a gaseous fuel which has minimal nitrogen-bound-to-carbon content. The same end-of-pipe controls used for gas fired units are generally applicable to oil fired units provided PM loading is not an issue.

End-of-pipe NO_x controls include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). In SCR, flue gas is contacted with gaseous ammonia in a catalyst bed converting the NO_x to N_2 and water vapour. Although increasing the amount of ammonia will improve the conversion and removal efficiency of NO_x , it can result in ammonia slip (i.e., residual, unreacted ammonia in the flue gas stream), which can be harmful to any downstream treatment units due to deposits and can also create visible plumes. There are also operational issues with maintaining catalyst activity.

Table 15 Controls to reduce NO_x emissions

Emission control	Relative cost
Install lower NO _x burners	Low
Steam injection	Medium
Flue gas recirculation	Medium
Substitute gas for liquid fuel	Medium
SNCR	High
SCR	Very high

Ammonia itself is an important pollutant and the amount of ammonia slip will have to be seriously considered and monitored.

In the SNCR NO_x reduction process, the conversion takes place completely in the gas phase at higher temperature without a catalyst. Good mixing of ammonia or urea and gas is essential for reasonable conversion efficiency. The SNCR process operates well within a relatively narrow temperature range set by the chemical used. SNCR is usually less effective than SCR in reducing NO_x in the flue gas.

Note that the pressure drop across combustion systems is a limiting factor for the use of secondary measures.

Cogeneration

Where power is generated on site, an option to improve efficiency that can be considered, which also reduces overall combustion emissions, is to generate both heat and electric power in one system. This is known as cogeneration. When generating power, some heat must be rejected to cooling. With cogeneration, this heat is used to generate steam or raise the temperature of a process fluid. The thermal efficiency of the system is much higher overall. Less fuel is consumed than would be the case in separate heating and power generation units, resulting in lower overall combustion and CO₂ emissions.

Good practices for control of boiler, heater and furnace emissions

- Reduce fuel consumption by applying energy conservation measures.
- Use lower sulphur containing fuels.
- Substitute gas for liquid fuel.
- Reduce sulphur in refinery fuel gas used in combustion units.
- Use 'low-NO_x' burner designs.
- Consider cogeneration opportunities when refurbishing on-site power generation or steam raising facilities.

Catalytic cracking

During the cracking reaction, some of the carbon in the gas oil feed is deposited as coke on the catalyst. This reduces catalyst activity, thus requiring that the catalyst be regenerated. The catalyst is circulated from the cracking reactor into a regenerator vessel where the coke is burned off to restore catalyst activity and reheat the catalyst. The heated catalyst is then returned to the reactor where it provides heating for the endothermic cracking reaction.

The catalytic cracker regenerator can be a significant source of combustion emissions. The combustion of coke during catalyst regeneration can result in SO_x, NO_x and PM emissions. The PM emissions can include catalyst dust as well as the PM from the coke combustion.

Sulphur oxides are created in the catalyst regeneration process when sulphur in the coke is burned. This sulphur originated in the feed to the cracker. The amount of SO_x emitted is directly proportional to the concentration of sulphur that is contained in the coke.

In the regenerator, nitrogen oxides are created when nitrogen and oxygen in the air combine at high temperatures (resulting in 'thermal NO_x') and

when elemental nitrogen in the coke is burned (resulting in fuel NO_x). In typical catalytic cracking operations, the fuel NO_x fraction of NO_x emissions is much greater than thermal NO_x due to the high quantity of fuel-bound nitrogen in the gas oil feed to the catalytic cracker.

PM emissions from the catalytic cracker can be both primary PM and secondary PM. There are two sources of primary particulate: cracking catalyst and soot from incomplete combustion. Secondary particulate (e.g. aerosols of NH_3 and SO_x) can be the larger fraction of particulate emissions after the primary cyclones collect and return most of the catalyst fraction. The quantity of secondary PM identified as being emitted as aerosols is defined by the condensing temperature of the flue gas sampling system.

How to quantify emissions

The most appropriate way to quantify emissions from catalytic cracker regenerators is to conduct stack test measurements at different operating conditions.

Sometimes it is possible to develop a parametric emissions model based on the stack testing for a specific unit. These models use test data from the unit to correlate emissions to changes in operating conditions. The model can then be used to help evaluate how changes in operations may impact emissions.

Choosing the best combination of emission controls for a catalytic cracker can be a complex process. Many of the end-of-pipe controls discussed above for furnaces, heaters and boilers are applicable to cracking regenerators. While these controls can be used to address only one of the pollutants, it is desirable, if possible, to use controls that can address at least two of the pollutants to reduce both capital and operating costs.

One combination control option that has been used is a wet gas scrubber for both PM and SO_x reduction in combination with additives used for NO_x reduction. Another control option is to use an electrostatic precipitator (ESP) for PM reduction with additives used for NO_x control. The potential to reduce SO_x emissions with additives should be explored together with the reduction of PM emissions using multi-stage cyclones. Where lower NO_x emission levels are required, SCR and SNCR units have been used but applicability and the cost-effectiveness for these techniques are poor. Dust must be removed upstream of the reactor. As for combustion, it may be noted that the pre-treatment of liquid fuel by hydroprocessing can reduce feed sulphur content and remove some metals, but this measure is not an abatement step per se. Investments in feed pre-treatment will be driven instead by the need to tailor the FCC product slate.

Table 16 provides an overview of the available emission controls for catalytic cracking units. It shows the available control options indicating which

Table 16 Control option applicability for catalytic cracking units

Pollutant	Control options							
	Cyclones	Fabric filters	Electrostatic precipitator (ESP)	Wet gas scrubber (WGS)	Feed pretreatment	Additives	Selective non-catalytic reduction (SNCR)	Selective catalytic reduction (SCR)
PM	●	●	●	●	–	–	–	–
SO_x	–	–	–	●	●	●	–	–
NO_x	–	–	–	●	●	●	●	●

pollutants can be addressed. Several of the options can be used for controlling more than one pollutant.

PM (particulate matter) control

The first step in PM emissions reduction is to use cyclones to disengage the larger catalyst particles. Most existing units already do this since there is a cost saving associated with reducing excessive catalyst loss. Multi-stage cyclones can sometimes achieve sufficient PM removal efficiencies so that no other controls are required. Tertiary cyclones have been used to achieve greater recovery of primary PM but with increased system pressure drop.

Wet gas scrubbers are an option when cyclones alone will not meet the PM control limit. If necessary, the WGS can be designed to also control SO_x emissions using an appropriate sorbent. New developments indicate that it is possible to also reduce NO_x emissions in a wet gas scrubber but the technology has not yet been applied commercially.

Wet gas scrubbers necessarily emit water vapour that can appear as a significant white plume that is clearly visible.

Electrostatic precipitators (ESPs) can be used to reduce dust emissions. The efficiency depends upon the particle size distribution, the resistivity of the dust and the inlet dust loading. For high efficiency large ESP volumes and up to four fields may be needed. Space requirements for retrofit are likely to be limiting. There are explosion hazards associated with the use of ESPs during startup and shutdown periods so that operating permits must address operation of the FCC without PM control at such times.

SO_x control

The emissions of SO_x from cracking units can be controlled in three general ways. One is to reduce the quantity of sulphur in the feed entering the unit.

Although this may be achieved by hydrotreating the feed, this is very expensive. Hydrotreating the feed is usually considered as a process modification where there is a need to change the FCC product slate. Another, and preferred, SO_x control is to use additives to reduce the feed sulphur that deposits on the catalyst. In this case, the sulphur stays with the gas or liquid product streams from the cracker and is more readily handled in downstream process units. The third way is to apply end-of-pipe controls such as scrubbers.

With existing units, the first option to consider is the use of SO_x reduction additives. This is often the least expensive control option and, in some cases, can provide the necessary emissions reduction. Additives can also play a role even if feed treating or end-of-pipe controls are necessary since they can often reduce the size or operating cost of these units. It is very difficult, however, to predict performance of these additives. Several vendors offer a range of different additives. Therefore, a trial period is essential to determine how well the additives will work in a specific application under different operating conditions.

NO_x control

The emissions of NO_x from cracking units can be controlled in three ways. One is to treat the feed to remove some of the chemically bound nitrogen. Again, this is not a preferred option. Another is to use NO_x reduction additives. Finally, there are the end-of-pipe controls such as SNCR and SCR, which are generally not cost-effective options due to the large investments needed compared to the NO_x removal achieved. With existing units, the first option to consider is the use of NO_x reduction additives. This is often the least expensive control option and produces useful reductions in emissions.

Additives can play a role even if end-of-pipe controls are applied since they can often reduce the size or operating cost of these units. However, it is

very difficult to predict performance of additives. Several vendors offer different additives. A trial period is essential to determine how well they will work in a specific application.

Good practices for control of catalytic cracker emissions

- Use cyclones to control emissions of larger particles and to return catalyst to the regenerator.
- Consider the use of additives for NO_x and SO_x emission reduction.
- Consider end-of-pipe equipment that can control more than a single pollutant.

Sulphur plants

Refinery gas streams contain hydrogen sulphide. It can enter as a by-product of processes that remove sulphur from unit feeds and products. It can also enter from sour water stripping. The potential SO_2 emission can be reduced if the H_2S is removed from such gas streams by, for example, amine treating prior to their addition to the refinery fuel gas system. Not all gas streams need to be treated in this way and the final refinery fuel gas sulphur content will be the result of blending. The H_2S removed from the refinery fuel gas supply streams needs to be routed to the sulphur recovery unit where it is destroyed and sulphur recovered as a solid product.

How to quantify emissions

Any sulphur in gases that are combusted is assumed to form SO_x . Material balances that track total sulphur content of the sour gases, amount of sulphur recovered and amount in combusted gases will provide sufficient information to calculate emissions with and without controls.

Periodic sampling of fuel gas for total sulphur is recommended. Stack sampling of sulphur plant tail

gas emissions will also provide improved quantification of SO_x emissions.

Sulphur recovery

Hydrogen sulphide can be removed from gas streams using chemical solvents, physical solvents or dry adsorbents.

Amine absorption

Many gas treating processes in refineries use amines to absorb the H_2S . The choice of amine and system operating pressure will determine the energy consumption and the removal efficiency.

In an amine treating unit, H_2S is absorbed from the fuel gas stream and cleaned fuel gas is sent to the refinery fuel gas system. The contaminated amine is sent to a regenerator for removal of H_2S . The cleaned amine solution is then returned to the absorber to repeat this cycle. The concentrated H_2S gas next goes to the sulphur recovery unit.

Sulphur recovery units

Most refineries use the Claus process to convert the concentrated H_2S stream from the amine treating unit into elemental sulphur. In the Claus process, the gas stream containing the H_2S is burned, producing SO_2 . The combustion gas then goes through a reactor where it is reduced to elemental sulphur. The sulphur is condensed and separated as a liquid. There are usually two or three stages of this reducing reaction depending on the desired level of conversion to elemental sulphur.

The 'tail gas' from the Claus plant will still contain a small amount of unconverted SO_2 , H_2S and some organic sulphides. For additional sulphur reduction, some refineries use a tail gas clean-up unit. These may provide further absorption using amines or combustion and catalytic conversion. The conversion of the third stage of a three-stage Claus system to a tail-gas unit, using 'SuperClaus' technology, is a common option, and can achieve up to 99.3% sulphur recovery. Other technologies

are needed to achieve higher overall efficiencies, but at more significant cost. Many locations send the gas from the Claus unit directly to an incinerator if residual sulphur concentrations are low enough to allow this option.

Other, smaller, potential H₂S emission sources associated with the sulphur recovery process include sulphur collection pits and sulphur storage tanks. Emissions from these units may also need to be controlled. In some cases, it may be more economical to collect and incinerate these H₂S-containing gases and, if necessary, to use end-of-pipe controls to reduce the resultant SO_x emissions.

Good practices for control of sulphur plant emissions

- Periodically sample sulphur content of refinery fuel gas.
- Avoid using high sulphur containing gases as fuels.
- Concentrate H₂S streams using recovery units such as amine scrubbers.
- Recover sulphur using Claus or other processes.
- Collect and treat off-gases from sulphur pits and sulphur storage tanks.
- Monitor sulphur plant stack emissions.

Gas turbine NO_x

As with other combustion sources, NO_x controls for gas turbines either reduce NO_x generation by reducing combustion temperatures or by removing NO_x from the flue gas using end-of-pipe controls. The most widely used method to reduce NO_x generation is steam injection. This reduces the combustion temperature. The most widely used method to remove NO_x from flue gases is selective catalytic reduction (SCR).

Flares

Flares are a widely used control device for reducing the emissions of hydrocarbon vapours. As plants have become more environmentally efficient, the amount of routine flaring has been significantly decreased and most of the emissions are from episodic (upset) events. When the gases are combusted they produce NO_x and PM and, if any sulphur compounds are present, SO₂.

There is an emission factor in AP-42 (US EPA, 1995b) for estimating NO_x from flaring. There are several factors in AP-42 for primary PM (soot) depending on the amount of smoking observed. These emission factors have high uncertainty because of differences in flare design and gas composition. Emissions of SO_x can be determined by 'material balance' assuming all of the sulphur species are completely oxidized.

Source reduction

The most effective way to control flare emissions is to minimize the material sent to the flare. Improved operation of processes to reduce potentially vented material that is flared, as well as recycling vented material back into the process system are options. Some plants have initiated a 'flare minimization plan' to focus efforts.

Flare minimization plans generally include a listing of measures to address flaring as a result of planned major maintenance. This includes minimizing gas sent to the flare during startup and shutdown operations. It also includes identifying methods to reduce flaring caused by failure of air pollution control equipment, process equipment, or processes.

Gas recovery

Flare gas recovery is a system designed to collect the hydrocarbon vapours that are sent to the flare and process them so that they can be returned to

the process or utilized as fuel. The system includes pipe headers to collect the gases and condensers to remove any liquids. When the gas is used as a fuel, the system includes a compressor to introduce the gas into the fuel gas system.

Although there is some economic benefit when the recovered gas is used as fuel, these systems are generally not cost-effective. They can be quite expensive if there is need to transport waste gases from widely separated areas within a plant or if there are significant impurities in the gas that must be removed prior to use as a fuel.

Odour control and management

This section focuses on the management of odour. It does not address the public communication necessary in the event of a major accident resulting in the bulk release of hazardous chemicals and the consequent liaison with emergency services.

As an air emission odour presents special challenges. The source may not be known or readily identified. If the odour is detectable outside the refinery fenceline and there is a negative public reaction, the technical investigation needs appropriate public affairs support. Where odour events are intermittent rather than persistent, the successful location of the problem may depend critically on analysis of the public response.

There is usually a wide range in individual responses when people are exposed to an odorous compound. Each person may detect odours at a different concentration and there may not be a consensus on the degree to which an odour is considered objectionable. Some odours may even be considered pleasant. Habituation may reduce sensitivity to nuisance associated with an odour. Perceptions of a change in odour intensity may be particularly strong.

A process to address odour problems can be divided into four steps. The first is to assess the problem and establish the need for the facility to take action. This is followed by identifying the potential sources of the odorous material both within and external to the plant (some sources have been found to be external to the plant that received a complaint). Analysis of the potential sources and reported impact is then used to confirm the location of the release and that it is the cause of the odour problem. Finally, emission reduction actions are considered to bring the ambient concentration to levels below the odour detection limit.

Problem assessment

To a substantial degree, the information needed to assess an odour issue will comprise reports from the public, and an appropriate infrastructure is needed to handle and record, in a factual manner, information that is very likely communicated by telephone. The same infrastructure can also work to handle reports from on-site personnel, and operational issues that create temporary odour sources should be reported and recorded as soon as possible. It is also important to provide feedback to the public, and a means of recording information provided, including details of when and to whom the information was given, should be included.

The first information needed to assess an odour problem includes: the time and date of the call and the identity and contact details of the reporter; the time and date that the odour was noticed; the location at which the odour was noticed; the distinguishing characteristics of the odour; and any knowledge of the chemical and its source.

This time and location information will be needed to cross-reference with information on wind-speed and direction, general weather conditions, etc., and with information on plant operations during the relevant time, as an attempt to locate the source.

Where there is enough information to confirm and explain the source of odour, and if the cause has been recognized and quickly remedied, the problem may be considered solved and appropriate feedback given.

When progressing to source identification, the possibility that the source arises from outside the facility should be considered. Where the potential is high, for example in a manufacturing complex with several operators, a coordinated approach may be appropriate.

Source identification

Once the need for action has been established, steps are taken to identify the emission sources that are causing the odours. Based on the odour, it is often possible to identify specific chemicals and potential sources within the plant. Plant personnel may be able to determine the probable process units where the odour is originating since they are likely familiar with odours associated with specific process units. Many classes of chemicals have distinctive odours that are easily recognizable (CONCAWE, 1975). In some cases, analysis of air samples may be necessary to identify or confirm the chemicals involved. At this point, the likelihood of any potential hazards associated with exposure of plant personnel or the community to the suspected chemical should be determined. Adequate safeguards should also be in place to detect releases of hazardous materials (e.g. H_2S), together with appropriate emergency response planning.

When the chemicals causing the odour have been identified, a list of locations in the plant where these chemicals may exist should be created. These locations are then surveyed to determine whether they are the source of emissions contributing to the odours reported. The location, wind direction and timing of the odour reports should be examined to determine whether specific plant areas may be the emission source.

There may be several plant sources that are contributing to an odour. Emissions from all sources may not need to be reduced to solve the odour problem. While it is necessary to reduce the ambient concentration of the chemical to below the odour detection threshold, a cost-effective solution may be to focus on the most appropriate source to remedy. This may be guided by carrying out an impact assessment.

Impact assessment and verification

In this step, the ambient concentrations of the odour-causing chemicals are quantified to help focus emission reduction efforts on the most appropriate sources. This can involve ambient air monitoring in the community surrounding the plant, or emissions estimating combined with dispersion modelling to predict concentrations. Actual or predicted ambient concentrations are then compared to odour detection thresholds and the locations of odour complaints; this provides a better understanding of the source contributions and allows odour reduction efforts to be focused appropriately.

Table 17 provides odour detection thresholds, published exposure limits and odour descriptions for some common industrial chemicals. Plants should check with their regulatory agencies for the latest local limits on ambient concentrations. Information on a wider list of chemicals is available in US EPA, 1992. The plant industrial hygienist should be consulted to confirm acceptable exposure limits for both plant personnel and the community.

The lack of a relationship between odour detection thresholds and recommended exposure limits can be demonstrated using the information in Table 17. Hydrogen sulphide has a much lower odour detection threshold than its exposure limits. This is a chemical that will be detected at much lower concentrations than will cause any health or safety issues, but this might not be understood by the public.

An opposite example is ammonia, where the odour detection threshold and the exposure limit are relatively close. In this case, odour detection is an indication of a potential health hazard. Table 17 shows that there are even some chemicals where the odour detection threshold is well above the recommended exposure limit.

Table 17 Example odour detection thresholds, exposure limits and descriptions

Chemical	Odour threshold (ppm)	Exposure limits (ppm)		Odour description
		TWA*	STEL†	
Acrylonitrile	1.6	2	10	Garlic/onion
Ammonia	17	25	35	Irritating/pungent
Carbon disulphide	0.0081	1	10	Sulphur
Chlorine	0.01	0.5	1	Bleach
Dimethyl amine	0.34	5	15	Fishy
Ethylene dichloride	26	1	2	Chloroform
Hydrogen sulphide	0.0005	10	15	Rotten eggs
Methanol	100	200	250	Sweet and sour
Methyl amine	4.7	5	15	Fishy
Methyl ethyl ketone	10	200	300	Sweet
Naphthalene	0.027	10	15	Tar
Styrene	0.047	50	100	Sweet
Sulphur dioxide	2.7	2	5	Irritation/pungent
Toluene	2.8	100	150	Sour
Trichloroethylene	82	50	100	Ether

*TWA: time weighted average—the allowable exposure level for a normal 8-hour day, 40-hour work week.

†STEL: short-term exposure limit—the allowable exposure level for short periods of about 15 minutes.

Dispersion modelling can usefully guide monitoring programmes provided that there is sufficient information available to reasonably quantify the emissions and account for the local meteorology. The model should be able to account for concentration fluctuations in order to reflect the short-time peak concentrations typical of some odour problems. The guidance that is most useful is for the location of monitors and the likely concentration ranges to be encountered.

Conducting an ambient air monitoring programme will generally cost much more than emissions estimating and dispersion modelling. In addition, monitoring has some limitations and care must be used in its application. When monitoring, it is possible to miss the odour plume by having too few monitors or by placing them in non-optimal

locations for the local meteorology. In addition to placing monitors in areas where there have been past odour complaints, typically expected wind directions should be considered when placing monitors, so as to increase the likelihood that any plant emissions will be detected.

In some cases, the odour detection threshold may be lower than the analytical detection method limit for the chemical. Monitoring may not always be of benefit in these cases. However, if the chemical is detected above the odour threshold, this provides confirmation of the problem and subsequent monitoring can be used to show successful elimination of the odour problem.

If emissions estimating and dispersion modelling of worst-case conditions show that certain sources

would not result in ambient concentration near the odour detection threshold, it may be possible to eliminate these sources from further consideration as primary sources. However, they may still need to be considered as secondary sources if they could cause perceptible odours when combined with other sources.

There is a need to consider combinations of several sources of the chemical which, in combination, may result in concentrations approaching or exceeding the odour detection threshold. Analysis will show which combinations of sources can be reduced to eliminate the odour problem. If there are alternative solutions, costs should be considered.

Problem resolution

Once the need for an odour control plan has been established, specific emission sources can be identified and applicable emission reduction techniques can be evaluated. Many of the emission reduction technologies discussed in this manual can be applied. Emission reduction opportunities should be evaluated based on the contribution of each source to the odour problem and the cost of the control.

The odour intensity of a specific chemical is related to the ambient concentration by Stevens' Law:

$$I = kC^n$$

where:

I = odour intensity

C = ambient concentration

K, n = constants

The value of the exponent in Stevens' Law ranges from about 0.2 to 0.6, with most sulphur compounds near 0.3. Thus, for example, a 50% reduction in the ambient concentration of a chemical with a Stevens' Law exponent of 0.3 would result in a perceived odour reduction of less than 20%.

Therefore, the emissions reduction required to achieve ambient concentrations below the odour detection limit will be greater than if the perceived odour intensity was proportional to the ambient concentration. A consequence is that emission reductions might require high cost investments.

Steven's Law exponents are only available for a limited number of chemicals. The reported exponents have some uncertainty since they were developed using different protocols and odour panels. Some Steven's Law exponents are provided in Table 18. If no exponent is available for a chemical of concern, the use of 0.3 is recommended in initial evaluations.

Where there is no clear option to eliminate odour sources on a short time scale, alternative emission reduction approaches should be discussed in consultation with the public focal points. Consideration should also be given to balancing reductions of odour intensity with reductions of odour impact frequency. In some cases, it may be advantageous to decrease the frequency of the odour rather than the strength of the odour. This may be acceptable to the surrounding community and may be beneficial for the plant since the frequency of odour problems can often be reduced at lower cost through improved operations and housekeeping.

Table 18 Exponents for Steven's Law equation

Chemical	Exponent
Acetaldehyde	0.26
Butyl mercaptan	0.29
Chloroform	0.58
Ethyl mercaptan	0.25
Methyl mercaptan	0.34
Toluene	0.53

Good practices for addressing odour problems

- Operations personnel should monitor for odours and report them promptly.
- Keep surrounding community fully engaged.
- Identify potential odour sources outside the plant.
- Compare actual impact areas with predictions from emission and dispersion modelling.
- Consider maximum short-time concentrations when evaluating impacts.
- Remember that the technical solution may not always satisfy the surrounding community.

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