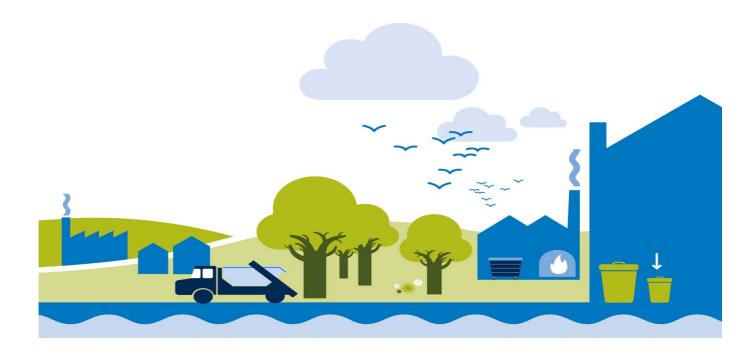


How to comply with your environmental permit Additional guidance for:

# Gasification, Liquefaction and Refining Installations (EPR 1.02)



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#### Introduction

In "Getting the basics right – how to comply with your environmental permit" (GTBR) we described the standards and measures that we expect businesses to take in order to control the risk of pollution from the most frequent situations in the waste management and process industries.

This sector guidance note (SGN) is one of a series of additional guidance for Part A(1) activities listed in Schedule 1 of the Environmental Permitting Regulations (the Regulations). We expect you to use the standards and measures in this note <u>in</u> <u>addition</u> to those in GTBR to meet the objectives in your permit.

Sometimes, particularly difficult issues arise such as problems with odour or noise. You may then need to consult the "horizontal" guidance that gives in depth information on particular topics. Annex 1 of GTBR lists these.

The IPPC Directive requires that the Best Available Techniques (BAT) are used. When making an application, explain how you will comply with each of the indicative BATs in this sector guidance note. Where indicative BAT is not included, where you propose to use an alternative measure or where there is a choice of options you should explain your choice on the basis of costs and benefits. Part 2 of Horizontal Guidance Note H1 Environmental Risk Assessment (see GTBR Annex 1) gives a formal method of assessing options which you should use where major decisions are to be made.

We will consider the relevance and relative importance of the information to the installation concerned when making technical judgments about the installation and when setting conditions in the permit.

Modern permits describe the objectives (or outcomes) that we want you to achieve. They do not normally tell you how to achieve them. They give you a degree of flexibility.

Where a condition requires you to take appropriate measures to secure a particular objective, we will expect you to use, at least, the measures described which are appropriate for meeting the objective. You may have described the measures you propose in your application or in a relevant management plan but further measures will be necessary if the objectives are not met.

The measures set out in this note may not all be appropriate for a particular circumstance and you may implement equivalent measures that achieve the same objective. In cases where the measures are mandatory this is stated.

In response to the application form question on Operating Techniques, you should address each of the measures described as indicative BAT in this note as well as the key issues identified in GTBR.

Unless otherwise specified, the measures and benchmarks described in this note reflect those of the previous Sector Guidance Note. They will be reviewed in the light of future BREF note revisions. In the meantime we will take account of advances in BAT when considering any changes to your process.

#### Installations covered

This note applies to activities regulated under the following section of schedule 1 of the Regulations:

Section 1.2, Gasification, liquefaction and refining activities, Part A(1)

- Refining gas where this is likely to involve the use of 1,000 tonnes or more of gas in any period of 12 months.
- b) Reforming natural gas.
- NOT INCLUDED Coking (Refer to IPPC S2.0-1 Guidance for the production of Coke, Iron and Steel (2004))
- d) Coal or lignite gasification.
- e) Producing gas from oil or other carbonaceous material or from

mixtures thereof, other than from sewage, unless the production is carried out as part of an activity which is a combustion activity.

- f) Purifying or refining any product of any of the activities falling within paragraphs (a) to (e) or converting it into a different product.
- g) Refining mineral oils.
- h) The loading, unloading or other handling of, the storage of, or the physical, chemical or thermal treatment of crude oil; stabilised crude petroleum; crude shale oil; where related to another activity in this paragraph any associated gas or condensate and emulsified hydrocarbons intended for use as a fuel.
- The further refining, conversion or use of the products of any activity falling within paragraphs (g) or other than as a fuel or solvent
- j) Activities involving the pyrolysis, carbonisation, distillation, liquefaction, gasification, partial oxidation, or other heat treatment of coal (other than the drying of coal), lignite, oil, other carbonaceous material or mixtures thereof otherwise than with a view to making charcoal. (covered under Combustion Guidance Note S4 HOLD)
- k) Odorising natural gas or liquefied petroleum gas where that activity is related to a Part A activity

#### **Directly Associated Activities**

The installation will also include directly associated activities which have a technical connection with the main activities and which may have an effect on emissions and pollution, such as:

- the storage and handling of raw materials
- the storage and despatch of finished products, waste and other materials
- the control and abatement systems for emissions to all media
- waste treatment or recycling.

#### **Key issues**

The Refinery Sector covers the range of oil and gas energy industries. Activity is centred upon the refinery operations. Refineries manage large quantities of raw materials and are also intensive consumers of energy and water. Refineries generate large quantities of emissions from the storage and processing operations. The industry is mature and pollution control is part of ongoing developments. However, because of the nature of the industry, developments often need to be planned several years ahead of implementation to coincide with planned shutdowns of plant. As a result of investment, the emissions generated by refineries have declined per tonne of crude processed and are continuing to decline.

Refineries tend to process a comparatively narrow range of crude oil slates and the type and quantity of emissions are usually predictable. Sometimes, processing different crudes can have unforeseen impacts on the performance of the refinery leading to an increase in emissions.

#### **Emissions to air**

Power plants, boilers, heaters and catalytic cracking are the main sources of emissions of carbon monoxide and dioxide, nitrogen oxides (NOx), particulates, and sulphur oxides (SOx) to the atmosphere. Sulphur recovery units and flares as well as catalyst changeovers and cokers also contribute to the emissions.

#### **Energy efficiency**

Refinery processes require a lot of energy; typically more than 60 % of refinery air emissions are related to the production of energy for the various processes. Other installations in the sector are very significant net generators of energy. Many installations will be participants in a Climate Change Agreement or have an Emissions Trading Scheme permit

#### **Emissions to water**

Water is used intensively in a refinery as process water and for cooling purposes. Its use contaminates the water with oil products mainly increasing the oxygen demand of the effluent. Refinery waste water treatment techniques are mature

techniques, and emphasis is now on preventing and reducing the emissions.

#### Waste

The amount of waste generated by refineries is small compared to the amount of raw materials and products processed. Oil retained in sludges or other type of wastes represents a loss of product and, where possible, efforts are made to recover it. Waste disposal depends very much on its composition and on the local refinery situation. Waste minimisation is increasing. The Landfill Directive may require specialist pre-treatment of residues before they can be landfilled.

#### Soil and groundwater contamination

Most refineries have some contaminated areas. Current refinery practices are designed to prevent spillages and leaks to ground and remediate historical contamination. Most oil fractions are biodegradable, given time. 'Clean up' now comprises managing the risks of these contaminated sites to ensure their fitness for use and ensuring that pollution does not spread beyond the site.

Storage, transfer, and transport of hydrocarbons or of hydrocarbon containing water poses the greatest risk of groundwater and soil contamination. Contamination by other substances such as contaminated water, catalysts and wastes also exists.

#### Odour

Some of the substances produced or used have the potential to cause offence to neighbouring communities. This is a key issue for some installations, though probably not for the majority in the sector.

#### Noise and vibration

Noise and vibration are constant features of most refineries - from compressors and other machinery, steam relief valves, large combustion units, flares, etc.

#### Other environmental issues

Issues such as noise, light (flaring at night), smell and emission such as from flaring and condensing plumes which directly impact nearby residents are a priority for discussion with both local authorities and representatives of the local population. Visual impact is also important.

Increased attention, training, safe design and adequate tools and personal protection equipment has resulted in a steady decrease in the number of unsafe acts, accidents, incidents and near misses. Typical refinery pollutants and products with a health risk include

hydrogen sulphide, BTEX (of which benzene is the most prominent), ammonia, phenol, HF, NOx, SOx and particulates (including metal components), for which legally binding Maximum Acceptable Concentrations values exist. Adequate provisions for safe shut-downs and dealing with emergencies are crucial to minimise environmental and health and safety impacts.

# 1 Managing your activities

- **1.1 Accident management**
- 1.2 Efficient use of raw materials and water
- 1.3 Avoidance, recovery and disposal of wastes
- 1.4 Odour

### Accident management Efficient use of raw materials and water

#### 1. Managing your activities

#### **1.1 Accident management**

#### **Indicative BAT**

You should, where appropriate:

- Design process control systems to include provisions for a safe shut-down with minimum emissions from the unit involved. During unplanned operational upsets, these provisions should guarantee that feed supply is controlled or terminated followed by preprogrammed automated activating of pumps, relief systems, purging systems, flares and other equipment. Where necessary for key plant an uninterrupted power supply should be guaranteed.
- 2. Have standing emergency procedures to address emergency situations which could lead to direct spills occurring in parts of the plant which are neither fully contained nor fully automated (such as pipeline or tank bottom rupture). These will minimise and contain the spills, followed by rapid clean-up.

#### 1.2 Efficient use of raw materials and water

Aqueous effluent treatment is an "end of pipe" operation intended to re-cycle recoverable oil and produce an acceptable release to water from a combined process effluent derived from many refinery processes and other sources. An important technique for controlling releases is to minimise and regulate inputs at source by all available means. Implementing such measures and others has reduced total dry weather flow and storm design flow from the uncontrolled situation by up to 30%, as well as reducing and evening out the pollutant load reaching the treatment plant.

### Efficient use of raw materials and water Avoidance, recovery and disposal of wastes

#### Indicative BAT

You should, where appropriate:

- Implement water use management programmes, facilities and training to prevent or reduce excessive use, accidental spills and leaks, including arrangements to transfer known spillages or leaks directly to oil recovery processes, not via the drains. E.g. using tankers to draw light hydrocarbons from drain traps and manholes;
- 2. Recycle and re-use water, materials and reagents wherever possible. Examples include desalting where fresh water can be replaced by an appropriate re-cycled stream depending on the operating pH, crude oil will absorb dissolved pollutants;
- 3. You should assess the costs and benefits of using membrane techniques to minimise water use and effluent discharge;
- 4. Modify or adjust effluent-producing processes, especially those producing occasional intermittent "spikes" of high pollutant concentration that may damage or destroy the biomass. These include strong sources of phenols and sulphides, for example crude tank drainings, and their flow should be restricted and evened out. The design and operation of sour water strippers is another key element in minimising pollutant loadings, especially of sulphides and ammonia;
- 5. Separate and treat different effluent sources, eg non- contaminated/contaminated or process/non-process streams. This is an important factor in the optimum design and operation of successful refinery effluent treatment;
- 6. Install and use improved oil recovery systems such as slops plants.

#### 1.3 Avoidance, recovery and disposal of wastes

On-shore oil production and natural gas refining give rise to relatively small quantities of process wastes for disposal to land. They include occasional disposals of spent catalysts, activators, corrosion inhibitors, absorbents, adsorbents, filter cartridges and separator dusts; they may be contaminated with trace amounts of hydrocarbons. Desalinating a glycol purge stream gives rise to solids for disposal and any residual glycol in these should be reduced. Re-using recovered salt from desalination in off-shore drilling fluids may be possible. Plant maintenance cleaning and overhaul also generates waste requiring disposal, eg sludges and scale, and these may contain hydrocarbons and, in some cases (eg condensate reboilers), radionuclides.

On a complex refinery with fully developed effluent treatment, over 60% of the sludges typically arise from the effluent treatment. Boiler treatment sludges, tank bottoms, desalters sludges and oil spills make up most of the remainder.

The principal source of waste from raw materials in coal gasification is collected particulate matter from handling and processing of solid feedstocks. All coal dust is recycled to the gasifier. Some solid wastes may have value, e.g. certain spent catalysts are low grade fertilisers and other wastes may be used by other industrial processes, e.g. the aluminium industry can accept aluminium fluoride and some alumina-based catalysts.

The following table lists types of refinery solid waste, their typical origin and their typical disposal method:

Unit	Waste type and composition	Typical disposal method	Comments
Desalting units, lead additive units, some storage tanks	Desalter sludge and other sludges containing heavy metals such as nickel, vanadium and lead	Classed as special wastes; require disposal at appropriate licensed site	
Desalting units associated with crude oil distillation unit	Desiccant	Landfill	
Reformer	Platinum catalysts	Off-site metals recovery	
Hydrotreater	Nickel-molybdenum catalysts	Off-site metals recovery or landfill	Periodic disposal; option chosen depends on market for nickel/molybdenum and economics of recovery process
Isomerisation unit	Platinum catalysts	Off-site metals recovery	Periodic
FCC unit	Catalyst residues	Landfill	
Fluidised catalytic cracking unit	Catalyst fines comprising silica-alumina catalyst contaminated with vanadium and oil	Landfill	Drummed and secured before being transported off-site

Polymerisation plant	Catalyst	Landfill	Neutralisation prior to landfill disposal
Tankage	Sludge	Landfill	Centrifugation applied prior to disposal
Effluent treatment plant	Oily sludge	Biological treatment on site or incineration or disposal off site	Centrifugation prior to disposal to remove oil (as high as 10%)
Copper sweetening unit	Copper chloride catalyst	Landfill	
Hydrotreater	Hydrotreater catalyst	Off-site metals recovery	Careful handling to remove the catalyst under dry, inert nitrogen vacuum
Hydrofiners	Cobalt-molybdenum catalyst	Off-site metals recovery	
Amine regeneration unit	Reclaimed amine sludge	Incineration at hazardous waste facility	
Various units	Coke	Landfill/incineration / power generation	
Sulphur recovery unit	Activated alumina	Landfill	Infrequent
Sulphur recovery unit	Sulphur	Landfill/commercial outlet	
Combustion units	Soot/ash	Landfill	
Combustion units	Refractory metals	Landfill	Periodic: generated during shut down and maintenance phases
Combustion units	Alum sludge	Landfill	
Water treatment resins	Resins	Landfill	
Tank storage and handling	Sludges	Landfill or land farm	Leaded sludges transported off site for disposal; other sludges can either be treated on land farm or sent to landfill
Offices, catering facilities	Domestic waste, offices, sewage etc	Landfill and to sewage treatment	Most refineries have their own sewage treatment units

#### Indicative BAT

#### Storage and handling

- 1. Provide dedicated areas for the holding and collection of solid waste, avoiding crosscontamination of wastes or the mixing of incompatible materials;
- Avoid storing wastes of particular environmental sensitivity, such as halogenated organics, unless the materials are fixed or otherwise rendered harmless. High temperature incineration may be a preferred option. All substances produced by the process and disposed of to land on or away from the site should be handled and conveyed to prevent spillage, dust release or the generation of odours;

#### Regeneration

3. Regenerate amine solutions, molecular sieves and catalysts on site to minimise quantities of waste disposed of. Or, they should be returned to the supplier or a third party for regeneration;

#### Sludges

- 4. Store sludges in sealed or covered containers in a secure and sealed bunded area pending on-site or offsite disposal. On-site disposal of sludges include incineration;
- 5. Minimise oily materials at source followed by appropriate processing to re-cycle as much of the hydrocarbons as possible and pre-concentrate the residual matter to reduce its volume before ultimate disposal. Oil recovery is possible if the sludge contains 10% or more w/w oil. Techniques for treatment include the following, typically used in combination:
  - filtration, by filter press or screen belt press. Filter aids may improve efficiency but will add to final cake volume, typically 14% of feed
  - settling by gravity, final volume typically >50% of feed
  - centrifuging, usually in a decanter type machine, final volume typically 16% of feed
  - hot processes, e.g. steam heating of recovered oils to break emulsions or sludges to dry sludges, with vapour condensation and hydrocarbon recovery. Waste heat may be used
  - solvent extraction to separate oil and inert solids, the solvent being recovered and recycled.
- 6. Return recovered oil to process, e.g. via the refinery slops system;
- 7. Consider using hot processes or solvent extraction to recover further hydrocarbons. A dry waste is produced which can be landfilled without further treatment or stabilisation;
- 8. Not use open techniques to degrade refinery sludge waste (landfarming). This activity would need to comply with the Landfill Directive;
- Carry out ultimate disposal of treated sludges by a method that minimises environmental impact and produces a usable product or recovers energy.
   Techniques include:

- chemical stabilisation by adding lime to give a hard material which may be used in civil engineering
- solidification using a cement/pulverised fuel ash process, followed by landfilling of the resulting blocks
- encapsulation in a stiff seamless jacket, followed by landfilling
- incineration, preferably with heat recovery, followed by landfilling of ash residues
- biodegradation using contained methods (e.g. aerobic/anaerobic digestion).
- 10. Design plant layout to ensure that any spillage of sludges can be collected and cannot enter any drainage system;
- 11. Treat sludges from ETP activated sludge processes accordingly. They are biologically active and may have some limited value as a soil conditioner;

#### Contamination of soil and groundwater

- 12. Provide hard surfacing in areas where accidental spillage may occur, e.g. beneath prime movers, in storage areas, and in loading areas. The surfacing should be impermeable to process liquors. This also applies to tank bund floors. This facilitates recovery and clean-up operations and prevents penetration into the ground. The organic sludges should be recycled for processing (e.g. by filtration, centrifuging);
- 13. Not allow potentially contaminated surface run-off to drain into the ground. Particular care is needed in areas of inherent sensitivity to groundwater pollution. Surface/above-ground drains are preferred to facilitate leak detection (and to reduce explosion risks).

### Efficient use of raw materials and water Avoidance, recovery and disposal of wastes

#### 1.4 Odour

Odour can be a significant issue for some processes and they should be designed and operated appropriately. This applies particularly to sour gas processes, where special care is needed when handling rich amine streams and also sour condensates. Also, when processing gas, which is sweet but contains traces of very highly odorous sulphur compounds. These are mainly natural mercaptans and even at very low concentrations they are foul smelling. They typically partition into the hydrocarbon condensate product, which should be handled very carefully and should be sweetened by a suitable process.

#### **Indicative BAT**

You should, where appropriate:

- 1. Vent all odorous releases regardless of size (e.g. instrument purge lines) via suitable traps;
- 2. Provide a blanketed fixed roof emergency tank for off-specification or unstabilised/unsweetened condensate;
- 3. Have closed effluent systems vented to flare;
- 4. Have arrangements to collect and treat any spills of unsweetened condensate immediately with sodium hydroxide.

# 2 Operations

- 2.1 On-shore oil production
- 2.2 Oil refining
- 2.3 Natural gas refining
- 2.4 Gasification
- **2.5 Utilities**

### **On-shore oil production**

#### 2. Operations

#### 2.1 On-shore oil production

**Water:** the main waste water streams are produced water and wash water. Produced water is highly saline water contaminated with free and emulsified hydrocarbons and suspended solids. Following treatment, this stream is reinjected into the crude oil reservoir and may be used to help maintain oil field pressures. Wash water is contaminated with hydrocarbons. Normally disposed of with the produced water.

#### **Indicative BAT**

You should, where appropriate:

- 1. Prevent or minimise the release of VOCs. Associated gas should be put to constructive use wherever possible;
- 2. Burn surplus sweet gas on sites other than isolated wellheads with only storage facilities, using a well designed enclosed smokeless ground flare or incinerator;
- Minimise the quantities of gas to be flared or incinerated by using best available techniques, including appropriate plant selection and design, operating methods and field management;
- 4. Provide a high pressure enclosed smokeless ground flare in the event of a major depressurisation on sites with complex gas handling or processing operations;
- 5. During planned depressurisations, minimise the quantity of gas released by depressurising as much as possible through the process before flaring the remaining gas;
- 6. Re-inject produced water into the same oilfield, either to a producing formation as part of the reservoir pressurising system or to a disposal well.

#### 2.2 Oil refining

#### Handling and storage of crude oil, liquid intermediates and products

**Air:** releases include hydrocarbons and sulphur compounds from storage vessels, handling operations, leakages from seals on pumps, valves and flanges, pressure relief valves, spillages, water discharges, sludge disposal and ballast water. Water: pollutants in waste water include dissolved and free (insoluble) hydrocarbons, suspended solids, phenols, sulphides, chlorides, cyanides, ammonia and certain heavy metals.

**Land:** hydrocarbon contaminated sludges from storage tanks.

#### Indicative BAT

You should, where appropriate:

- 1. Reduce the need and numbers of required tanks through improved production planning and more continuous operations;
- 2. For external floating roof tanks, use a good (high efficiency) primary seal, such as a metal shoe or ring type mechanical seal or a product mounted encased liquid or resilient foam type seal, combined with a rim mounted secondary seal which also acts as a weather shield;
- 3. Reduce emissions from fixed roof tanks emissions by
  - installing an internal floating roof
  - using blanketing and consider increasing storage pressure
  - applying vapour recovery in stationary use and during loading/unloading
  - enhance vapour balancing and back venting during loading/unloading processes.

#### Crude oil atmospheric and vacuum distillation

**Air:** releases will occur from pressure relief valves, poor containment in overhead systems, glands and seals on pumps, compressors and valves, flue gases from process heaters, de-coking vents from process heaters, venting during clean out and sour water and waste discharges. Water: pollutants are hydrocarbons from aqueous process streams from desalters, overhead condensers, spillages and leaks, and ammonia and caustic soda used in column overhead corrosion protection. In the Desalters, fresh and/or recycled water is used to wash soluble salts out of the crude oil and the waste water contains

high levels of salt, sulphides, ammonia and phenol. This is directed to the effluent treatment plant. In the Crude and Vacuum distillation units the condensed aqueous solutions are sent to the sour water stripper. This will contain sulphides, ammonia, small quantities of chlorides and hydrocarbons.

**Land:** solid wastes are sludges from cleaning out desalters and other vessels.

#### Indicative BAT

You should, where appropriate:

- 1. Maximise heat integration by selecting between:
  - designing highly integrated units (e.g. progressive distillation)
  - increasing heat integration between the atmospheric crude distiller with the vacuum unit or with other refinery process units. Techniques include applying energy optimisation analysis to the crude preheat train; increasing crude distillation column pumparounds and reboiling sidestrippers with a heat transfer oil rather than by side stripping.
  - applying advanced process control to optimise energy utilisation.

#### Desalting:

- 2. Use multistage desalters for new facilities;
- 3. Apply good desalting practices (multistage desalters and combined use of AC & DC fields, recycling in multistage desalters, use of low shear mixing devices, avoidance turbulence) that result in optimum downstream processing and wastewater quality;
- 4. Maximise the (re-)use of refinery water as desalting water.

#### CDU/atmospheric distillation:

- 5. Use as alternative to reprocess slop;
- 6. Recover sulphur compounds from CDU off gases.

#### Vacuum distillation:

- 7. Maximise the use of liquid ring vacuum pump and surface condensers in place of some stage steam jet ejectors on the vacuum tower overhead;
- 8. Minimise waste water flow/transfer of hazardous substances from vacuum pumps by appling water recycling/waste water-free techniques;
- 9. Recover sulphur compounds from off gases.

#### High TAN crudes:

- 10. Install a full range of corrosion monitoring, such as electrical resistance probes and Fe/Ni ratio monitoring;
- 11. Use suitable corrosion control or metallurgy.

#### Gas separation processes:

- 12. Enhance the heat integration with upstream plant streams using low-level heat streams;
- 13. Re-use the fuel gas used for the regeneration of molecular dryers.

#### Natural gas plants:

- 14. Use as fuel preferably gas of saleable quality;
- 15. Consider alternatives to direct releases of CO<sub>2</sub> particularly for large flows;
- 16. Dispose in an environmentally responsible way of mercury recovered from raw natural gas.

#### Odorising of natural gas or LPG:

17. For Gas Separation Processes, prevent any release of odorant to any environmental medium during storage and handling (e.g. blanket storage).

#### Hydrogen consuming processes

**Air:** releases are sulphur oxides, oxides of nitrogen, carbon oxides, smoke, grit and dust in flue gas from process heaters. Hydrocarbons and sulphur compounds may be released from pressure relief valves, leakages from flanges, glands and seals on pumps, compressors and valves, particularly on sour gas and sour water lines, venting during catalyst regeneration and replacement or during cleaning, sour water and waste discharges.

**Water:** releases include hydrocarbons and sulphur compounds from spillages and

leaks, particularly from sour water lines. Aqueous effluents arising from these operations contain high concentrations of hydrogen sulphide and ammonia. The effluent is fed to the sour water stripper before the effluent treatment plant. During hydrocracking a low-volume, dirty effluent is produced containing ammonia and hydrogen sulphide, which is directed to the sour water stripper (SWS).

**Land:** spent catalysts are the main source of solid waste.

#### **Indicative BAT**

You should, where appropriate:

- 1. Use heat recovery from high temperature process streams in waste heat boilers and power recovery in the high pressure units;
- Route gases containing hydrogen sulphide to amine absorption and thence to SRUs. Route waste waters containing hydrogen sulphide and N-compounds to appropriate waste water treatment;
- 3. Use on-stream catalyst replacement for high-metal feedstocks. Promote catalyst regeneration options;

- 4. Hydrotreat products where olefins and colour bodies need to be removed (new plants);
- 5. For Hydrocracking, design and retrofit (where possible) hydrocracker units (reactor and fractionation section) to highly heat integrated equipment, applying energy optimisation analysis and four-stage separator system.

### Gasoline production processes *Catalytic reforming*

Venting during catalyst regeneration or replacement and plant cleaning should use procedures that minimise releases. Emissions from continuous regeneration require scrubbing to reduce dioxin and hydrogen chloride releases where appropriate. Ozone depleting substances should not be used as catalyst promoters. Promoters should be handled in enclosed systems.

**Air:** releases include hydrocarbons from pressure relief valves and leakages. Hydrocarbons, dust and hydrogen chloride from venting during catalyst regeneration and replacement and during clean out operations. Flue gas from process heaters may contain sulphur oxides, oxides of nitrogen, carbon oxides, smoke, grit and dust. The storage and handling of organic chlorides may also lead to releases.

**Water:** releases are hydrocarbons from spillages and leaks.

#### Fluidised catalytic cracking

Fluidised catalytic cracking units (FCCUs) have the potential to release significant amounts of particulate matter, sulphur

dioxide, oxides of nitrogen and carbon monoxide. Operational and abatement options which can reduce releases of more than one pollutant will provide an advantage.

**Air:** releases are oxides of sulphur, oxides of nitrogen and carbon dioxide from the combustion of sulphur-containing fuels on the feed furnace and catalyst regeneration train. Incomplete combustion may release carbon monoxide, smoke and particulates if heavy fuel oil is used in the feed furnace. Particulate matter arises from catalyst fines from the catalyst regeneration exhaust gases and catalyst handling and disposal. Hydrogen sulphide and mercaptans may arise from sour waters from reflux condensers. Hydrocarbons from pressure reliefs, storage and handling operations, spillages and water discharges.

Water: releases are hydrocarbons and sulphur compounds from sour water drains and spillages. Sour water from the scrubber section containing phenols, ammonia, hydrogen sulphide and hydrogen cyanide, is routed to the SWS.

Land: solid waste comprises intermittent spent catalyst and particulate matter from abatement equipment, which contains catalyst.

#### Hydrogen fluoride alkylation

Air: releases are oxides of sulphur and nitrogen, and carbon dioxide from combustion of sulphurous fuels in the column-heating furnace. Incomplete combustion may lead to releases of carbon monoxide, smoke and particulates if heavy fuel oil is used. Hydrocarbons will arise from pressure reliefs, storage and handling operations, spillages and water and waste discharges. Halogens from pressure reliefs, vent gas and spillages. Acid soluble oil from process shut-down ponds during maintenance work. particularly the de-scaling of pipes conveying hydrogen fluoride. This may be odorous.

Water: aqueous wastes are hydrocarbons from separator drains (surge drum, accumulator, dryer) and spillages; acidic effluent containing dissolved and suspended chlorides and fluorides from the settlement pit or the process shutdown ponds.

**Land:** solid wastes comprise hydrocarbons from spent molecular sieves, carbon packings and acid soluble oil, and inorganic fluorides and chlorides from treatment stages.

#### Isomerisation

**Air:** releases are hydrocarbons from pressure relief on surge drums, separators

and column reflux drum, regeneration vent gas from dryers, storage and handling operations, spillages and water and waste discharges. Releases of hydrogen may occur from pressure relief on the hydrogen system.

**Water:** releases are hydrocarbons from reflux drum boot drain and spillages and spent sodium hydroxide from the scrubber system.

**Land:** solid wastes are hydrocarbons from spillages/contaminated molecular sieves and catalyst.

#### Catalytic polymerisation

**Air:** releases are hydrocarbons from pressure reliefs, storage and handling operations, spillages and water and waste discharges, and of particulate matter from catalyst fines from handling and disposal of spent catalyst.

Water: releases into water are of hydrocarbons from sour water purge from washtower, condenser drains and spillages, and particulate matter from spillages of catalyst fines.

**Land:** solid waste produced is solid acids and hydrocarbons from spent catalyst.

#### Aromatics production

**Air:** releases into air include hydrocarbons in the form of incondensibles from fractionating column overheads, pressure reliefs, vacuum ejector vents, hotwells, handling and storage, spillages and water discharges.

**Water:** releases into water are of degradation products from solvent purge stream still, condensate from fractionating columns overhead condensers and spillages contaminated with hydrocarbons.

#### Etherification

**Air:** releases into air are as hydrocarbons from pressure reliefs on vessels, depentaniser column overheads drum and distillation column reflux drum, methanol plant, steaming vents on scavengers and reactors, spillages, water and waste discharges. Releases of hydrogen occur from the distillation column reflux drum.

**Water:** releases into water are of hydrocarbons, methanol, formic acid and TAME/MTBE from spillages and water bleed from methanol recovery.

**Land:** solid wastes are spent resins contaminated with hydrocarbons.

#### Indicative BAT

#### Catalytic reforming:

- 1. Route regenerator gas during catalyst regeneration to a scrubbing system and bleed stream from the scrubbing system to the ETP;
- 2. Optimise use of chlorinated promoters in regeneration of the catalyst;
- 3. Quantify dioxin emissions and consider dioxin clean-up techniques;

#### Catalytic cracking:

- 4. Include a CO furnace/boiler for partial oxidation conditions;
- 5. Monitor and control O<sub>2</sub> for full combustion plants;
- 6. Increase energy conservation by applying power recovery as an expander to the regenerator gas or using a waste heat boiler to recover energy content in the flue gas;
- 7. Reduce NOx emissions by modifying the design and operation of the regenerator, hydrotreating the feedstock, using SCR/SNCR on the regenerator flue gas;
- 8. Reduce particulate emissions by using tertiary and multistage cyclones, ESP or scrubber to the regenerator gas thereby, containing catalyst losses to atmosphere during loading/unloading, hydrotreatment of the feedstock, or by use of attrition-resistant catalyst. Consider techniques which reduce particulate matter and sulphur dioxide;
- Reduce SO2 emissions by appropriate combination of hydrotreatment of the feedstock, using DeSOx catalyst additive, wet FGD of the regenerator flue gas. Regenerative SO2 scrubbing technology offers distinct advantages in reducing raw materials usage and minimising both liquid and solid waste streams;
- Reduce discharges to water by hydrotreating the feedstock, minimising water use and/or applying cascading systems, re-using waste water in desalters or ultimately routing to ETP;
- 11. Reduce waste generation by selecting attrition-resistant catalyst and reducing uncontrolled catalyst losses;

- 12. For the FCCU, consider final stage electrostatic precipitation for improved existing processes, where only reductions in particulate matter releases are a priority;
- 13. For the FCCU, consider regenerative wet scrubbing and its ancillary processes for removing both particulate matter and sulphur dioxide for both new processes and improved existing processes;
- 14. Monitoring and control of excess oxygen, typically at about 2%, is BAT for controlling CO for full combustion type regenerators in the absence of a down stream CO boiler. Where a CO boiler is installed it should be carefully designed and operated to minimise CO and NOx releases. Partial combustion type regenerators usually produce less NOx in their flue gases, allow greater throughputs and heat/power recovery. They are considered BAT for new FCCUs;

#### HF alkylation:

 Using HF technique represents a potential major accident hazard. Associated with BAT is the reduction of regular HF emissions to levels < 1 mg/Nm3 by scrubbing, to levels of 20-40 ppm F in the discharges to water after AIF<sub>3</sub> or CaF<sub>2</sub> precipitation;

#### Sulphuric acid alkylation:

16. Minimise and regenerate the spent sulphuric acid. Waste water generated by this process should be neutralised before routing to the ETP;

#### **Isomerisation introduction:**

- 17. Use active chloride-promoted technology subject to performance levels. Optimise the use of chlorinated organic compounds;
- 18. Use other catalytic systems (e.g. Zeolite);

#### Catalytic polymerisation:

- 19. Optimise catalyst (Phosphoric acid) consumption;
- 20. Properly manage the unused on-site catalyst for disposal or re-use off site. Re-use phosphoric acid catalyst within the refinery as much as possible e.g. biotreater;

#### **Etherification:**

- 21. Apply heat integration either within the unit itself or within the refinery;
- 22. Use a storage tank or production planning to control waste water generated to prevent upset of the WWTP biotreater.

#### LPG recovery and sweetening Liquefied petroleum gas (LPG) production

**Air:** releases into air are of hydrocarbons from pressure relief on vessels, regeneration vent gas from molecular sieves, C1/C2 fuel gas, refrigeration system leaks, storage and handling operations, spillage and water/waste discharges.

**Water:** releases into water are of hydrocarbons from spillages.

**Land:** solid wastes are of hydrocarbons from contaminated spent molecular sieves.

### Chemical treatment (sweetening) processes

**Air/Water:** releases into air and water are of hydrocarbons and sulphur compounds from leakage, venting from pressure relief valves, spillages and venting of excess air. Systems handling spent caustic require particular care regarding sulphur compounds.

#### **Indicative BAT**

You should, where appropriate:

1. Incinerate the spent air from sweetening processes (as part of odour abatement programme);

#### Liquefied petroleum gas (LPG) production:

- 2. Integrate heat with upstream plants to make use of heat available from upstream plants;
- 3. Re-use fuel gas from hot regeneration of molecular sieve dryers;
- 4. Store and handle odorants to prevent emissions to the environment;

#### Chemical treatment (sweetening) processes – FCC merox & kerosene merox:

- 5. Minimise spent caustic releases by optimising the recycling process and where possible by "cascading";
- 6. Handle and dispose of spent catalysts to avoid dust generation. They should not be disposed of to land;
- 7. Incinerate foul air vented from sweetening processes in local furnaces.

#### Bottom barrel processes and lubes

#### Visbreaking (mild thermal cracking)

**Air:** releases into air are of oxides of sulphur, oxides of nitrogen and carbon dioxide from the combustion of sulphurcontaining fuels in the cracking furnace. Incomplete combustion may lead to releases of carbon monoxide and smoke, and particulates if heavy fuel oil is used. Hydrogen sulphide and mercaptans are released from the sour water stream from reflux condensers and from the acid gas stream from the amine unit. Hydrocarbons are released from pressure reliefs on reflux drums and vessels, storage and handling operations, spillages and discharges of waste/water.

**Water:** releases into water are of hydrocarbons and sulphur compounds from the sour water drain, from reflux drums and spillages.

Land: solid waste is hydrocarbons and sulphur compounds in spent amine solution sludges.

#### Petroleum coke production

**Air:** releases to air arise from the combustion of sulphurous fuels/feeds in the coking furnace, calciners and incinerator. Incomplete combustion releases carbon monoxide, smoke and particulates if heavy fuel oil is used. Incomplete combustion in the incinerator releases hydrocarbons. Hydrogen sulphide and mercaptans may be released from the sour water stream from reflux condensers. Hydrocarbons may be released from pressure reliefs on reflux drums and vessels, quench tower emissions, storage and handling, spillages and waste and water discharges. Particulates may be released from kiln gas cleaning, rotary cooler gas cleaning, coke handling and storage and loading operations.

Water: releases into water are of hydrocarbons and sulphur compounds from the sour water drain from reflux condensers and spillages, and of particulate matter from drilling, quenching, blowdown sump water, rotary cooler scrubber discharge and spillage. Aqueous condensate from the main fractionator contains high concentrations of sulphides and ammonia, as well as cyanides and phenols. Water used in removing the coke from the drum (sometimes termed drilling water) is filtered and usually recycled.

**Land:** solid wastes are hot oil blowdown sludges containing hydrocarbons.

#### **Bitumen production**

**Air:** releases to air are oxides of sulphur and nitrogen and carbon dioxide from the combustion of sulphurous fuels/feeds in the coking furnace, calciners and incinerator. Incomplete combustion releases carbon monoxide, smoke and particulates if heavy fuel oil is used. Incomplete combustion in the incinerator releases hydrocarbons. Hydrogen

sulphide and mercaptans may be released from the sour water stream from reflux condensers. Hydrocarbons may be released from pressure reliefs on reflux drums and vessels, quench tower emissions, storage and handling operations, spillages and waste and water discharges. Particulates may be released from kiln gas cleaning, rotary cooler gas cleaning, coke handling and storage and loading operations.

**Water:** releases into water are of hydrocarbons and sulphur compounds from the sour water drain from reflux condensers and spillages, and of particulate matter from drilling, quenching, blowdown sump water, rotary cooler scrubber discharge and spillage.

**Land:** solid wastes are of hot oil blowdown sludges containing hydrocarbons.

#### Lubricating oil production

**Air:** releases into air include sulphur oxides, oxides of nitrogen, carbon oxides, smoke, grit and dust in the flue gas from process heaters. Organic compounds may arise from solvent vapour extraction from the wax filters. Hydrocarbons, sulphur compounds and organic compounds may be released from pressure relief valves on the hydrofiner, solvent recovery systems and refrigerant systems; leakages from flanges, glands and seals on pumps, compressors and valves; venting from wax filters and during catalyst regeneration/replacement procedures and cleaning; sour process waters and waste discharges.

**Water:** releases into water are of hydrocarbons, sulphur compounds and organic compounds from spillages and leaks, and of organic compounds from process waters from solvent recovery operations.

**Land:** solid waste is spent hydrofining catalyst.

#### Indicative BAT

You should, where appropriate:

- 1. Use dry inertial (cyclone) techniques and fabric filters for particulate control;
- 2. Remove sulphur, nitrogen and oxygenated compounds by hydrofining, rather than sulphuric acid and clay treatment;

#### Visbreaking:

- 3. Apply deep thermal conversion, or soaker visbreakers;
- 4. Sweeten the gas from visbreaking. Treat gas & effluent water because of the presence of sulphur compounds. Transfer aqueous condensate in enclosed systems;
- 5. Reduce the coke formation by controlling the sodium content in the visbreaker feedstock or by using additives that decelerate the coke formation;

#### Petroleum coke production:

- 6. Use an enclosed hot blowdown system for the coking process;
- 7. Use waste heat boilers to recuperate heat produced during the coking/calcining process;
- 8. Consider flexicoking (fluid coking + gasification) to maximise production of fuel gas and increase heat integration;
- 9. Use coker as alternate to destroy slops & sludge;
- 10. Convert COS from the coke gas of flexicokers to H<sub>2</sub>S and route sour gas produced from cokers to sulphur treatment;
- 11. Reduce particulate emissions by collecting and recycling coke fines, by proper coke storage and handling, by covering conveyors and depressurising with filters, by enclosing loading areas and keeping under negative pressure with exhaust through filters or dust extraction associated with loading equipment, by flue gas treatment with ESPs, cyclones, filters;
- 12. Reduce SO<sub>2</sub> emissions from the calciner flue gas by FGD techniques;
- 13. Reduce emissions to water by using treated water from the waste water treatment as cooling/cutting water in the delayed coking/calciner process; by stripping waste water generated in coking processes before sending it to the WWTP;

#### **Bitumen production:**

- 14. Reduce aerosol and VOC emissions by recovering the liquid element of the aerosol that is directed to vents from storage and during blending/filling operations and/or incineration at a temperature over 800°C or in process heaters;
- 15. For bitumen blowing, treat the overheads from the oxidiser for removal of air contaminants (water scrubbing with water cleaned before re-use, incineration with blow gas used in process heaters), accumulate water condensate and send to sour water stripper, send condensed hydrocarbons to the slops or alternative recovery method;

#### Lubricating oil production – base oil production:

- 16. Use triple effect evaporation systems (where technically possible) in the solvent recovery sections of deasphalting, extraction and dewaxing process units;
- 17. Use N-methyl pyrrolidone (NMP) or furfural on existing as solvent in the aromatic extraction;
- 18. Use hydrotreating for clean-up of base oil streams and wax finishing. Clay treatment may be justified if product quality cannot be achieved by hydrotreating but produces solid waste;
- 19. Consider the application of a common hot oil system for solvent recovery systems to reduce the number of furnaces;
- 20. Review the possibility of waste water stripping from aromatic extraction before re-use.

#### Ancillary processes Odorising of natural gas or LPG

**Air:** releases into air include leaks or spillages of odorant and vapours displaced during tank filling or from thermal expansion of blanket gas. Also the products of incinerating or flaring displaced vapours, including a small release of sulphur dioxide when the odorant is burnt.

**Land:** solid waste such as materials used to absorb odorant spillage.

#### Sour water stripping

**Air:** releases into air are of hydrocarbons, sulphur and nitrogen compounds from sour water drains, pressure relief valves, vents from feed vessels, spillages and leakages from flanges, glands and seals on pumps and valves particularly from overhead systems.

Water: releases into water are from spillages and leakages, and of sulphur and nitrogen compounds arising from inadequate stripping performance. The feed streams contain varying quantities of hydrogen sulphide and/or low molecular weight mercaptans, ammonia, phenols and cyanides. The steam stripped effluent is either reused or sent to the effluent treatment plant.

#### Sulphur recovery

**Air:** releases into air are of hydrocarbons and sulphur compounds from pressure relief valves, spillages and leakages from flanges, glands and seals on pumps and valves particularly from sour/acid gas lines and rich amine systems. Discharges from the incinerator may contain sulphur compounds, mainly sulphur dioxide, from unrecovered sulphur, oxides of nitrogen from gas burning and ammonia destruction, smoke and particulates. Vents from liquid sulphur storage tanks may lead to releases of sulphur compounds. Failure of the sulphur recovery unit usually causes a large amount of sulphur to be released through the flare system.

Water: releases into water are hydrocarbons, sulphur compounds and nitrogen compounds from spillages and leaks, particularly from sour/acid gas lines and rich amine systems.

**Land:** disposal of spent catalyst (normally bauxite) and solid sulphur waste and spillages.

#### Indicative BAT

You should, where appropriate:

#### Hydrogen plant/production:

- 1. Consider use of gas-heated steam reforming technology for new plants, including recovery of heat from the steam reformer flue gas and heat integration around the solvent absorber and the methanator;
- 2. Recover hydrogen from the gasification processes of heavy fuel oil and coke if the technology is applied in the refinery;
- 3. Apply heat integration schemes in the hydrogen plant;
- 4. Use PSA purge gas as fuel gas within the refinery;

#### Odorising of natural gas or LPG:

- 5. For Gas Separation Processes, prevent any release of odorant to any environmental medium during storage and handling (e.g. blanket storage);
- 6. Use amine scrubbing for hydrogen sulphide capture. A combination of common and individual scrubbers may be required;

#### Amine treating:

- 7. Use regenerative amine process;
- 8. Re-use amine solutions wherever possible;
- 9. Reduce the concentration of H<sub>2</sub>S in the refinery gas to levels of 100 ppm or lower;
- Have sufficient capacity to allow for maintenance activity and operational upsets (e.g. have redundancy equipment, apply load shedding, emergency amine scrubbers, multiple scrubber systems);
- 11. Use a storage tank or production planning to control waste water generated, to prevent any upset of the biotreater;

#### Sulphur recovery:

- For new processes, use process designs that can give a proven recovery efficiency of at least 99.5% (based on acid gas feed to the SRU) at design throughput and at turndowns of 50% or less;
- 13. In a typical mixed feedstock UK refinery, use at least two parallel SRUs;
- 14. Apply a staged SRU including tail gas treatment;
- Have a SRU configuration with sufficient capacity for the H<sub>2</sub>S feed to the unit and to allow for scheduled maintenance activity to proceed every two years without significant increase of sulphur emissions;
- 16. Have a utilisation factor of at least 96% including major planned turnaround maintenance. The target is 100% availability for new plant. With parallel units operational strategies should optimise recovery efficiency and minimise sour gas flaring;

## Natural gas refining

- 17. Apply alternative H<sub>2</sub>S recovery/removal techniques (iron chelating, solvent extraction, NaOH absorption, molecular adsorption) in installations where H<sub>2</sub>S production is small;
- 18. Consider the potential of oxygen enrichment on the performance outcome of SRUs and the amount of sulphur recovered and its destination;
- 19. Use of state-of-the-art control and monitoring systems. Sulphur recovery plants should have levels of control at least equivalent to other refinery processes. Using a tail gas analyser linked to the process control system (feedback control) will aid optimum conversion being achieved during all plant operating conditions;
- 20. Produce an overall account or mass balance of sulphur-bearing streams.

#### 2.3 Natural gas refining

Air: releases to air are hydrogen sulphides, oxides of nitrogen and carbon from gas treatment; hydrogen sulphides, nitrogen and carbon oxides and organic compounds from acid gas processes. Nitrogen removal generates hydrogen sulphide, organics and nitrogen. Nitrogen and carbon oxides and organics are releases from gas compressing and treating condensate. Hydrogen sulphides, sulphur dioxide, nitrogen and carbon oxides and organics are released from flares and vents and gas storage sites.

**Water:** the main process waste waters are condensed steam from glycol or methanol regeneration plants, contaminated with glycol or methanol, hydrocarbons, amines and mercaptans. The steam has very high levels of biological oxygen demand (BOD) and chemical oxygen demand (COD). This may go to off-site disposal or to full effluent treatment. Contaminated effluent arises from site drainage (storm and fire water), ballast water from shipping, cooling water, boiler blowdowns and water treatment / demineralisation regeneration water.

Land: solid wastes comprise spent catalysts/adsorbents and sand/corrosion products from gas treatment and gas storage sites.

#### **Indicative BAT**

You should, where appropriate:

 Minimise frequency of pig/sphere use by operating sea-lines at high velocity where practicable, ie use "mist flow" conditions, minimise recovery of spheres by use of receivers holding several devices and use of vent receivers of high pressure gas to a low pressure part of the process for gas recovery by recompression, before opening for access to pig/spheres;

### Gasification

- 2. Use sectioned vent and isolation systems which minimise the volume of gas to be released or allow high pressure gas to be vented down by an enclosed header system to a low pressure part of the process for recompression;
- 3. For planned depressurisation (eg of the sea-line or process plant), minimise the quantity of gas released by venting down to as low a pressure as possible through the terminal process before flaring the remaining gas;
- 4. Gas streams with significant sulphur content should not be used as fuel;
- 5. Consider alternatives to direct releases of CO<sub>2</sub> particularly for large flows;
- 6. Dispose of mercury recovered from raw natural gas in an environmentally responsible way.

#### 2.4 Gasification

**Air:** releases include particulates and organics from raw materials and slag/ash storage and handling and form salt recovery operations. Gas handling generates particulates, oxides of nitrogen, sulphide and carbon, organic compounds, hydrogen sulphide and ammonia. Particulates, oxides of nitrogen, sulphur and carbon, and VOCs are released from the gas turbine. Water: water treatment wastes contain metals, solids, organic matter and acids/alkalis. Waste water treatment effluent contains solids, organics, acids/alkalis and ammonia. Boiler blowdown water contains solids, metals and acids/alkalis.

**Land;** solid organic compounds are sent for disposal.

### Utilities

#### Indicative BAT

You should, where appropriate:

- Where fuel and raw materials are delivered by sea, use self-discharge vessels or enclosed continuous unloaders. Otherwise, dust generated by grabtype ship unloaders should be minimised through a combination of ensuring adequate moisture content of the material as delivered, by minimising drop heights and by using water sprays or atomised mist at the mouth of the ship unloader hopper;
- 2. Intercept and treat run-off by settlement or other techniques. Arrangements should be made for monitoring the quality of the water discharged from the storage and blending areas where such discharges are in the vicinity of potentially vulnerable receptors;
- 3. Control emissions of NOx by a combination, as applicable, of:
  - combustion control systems
  - combustion temperature reduction
  - low NOx burners
  - over fire air
  - flue/exhaust gas recycling
  - reburn
  - water injection
  - DLN.
- 4. For coal and oil-fired plant, use low NOx burners where applicable. Coal-fired plant above 100 MWth should have Over Fire Air (or equivalent);
- 5. Natural gas-fired gas turbines should use dry low NOx burners.

#### **2.5 Utilities**

#### Fuel systems and combustion processes

**Air:** Main releases are stack gases containing oxides of sulphur, oxides of nitrogen, oxides of carbon and particulate matter (which can include metals).

Land: grit and dust and arisings generated from cleaning procedures are sent for disposal.

#### **Indicative BAT**

You should, where appropriate:

- 1. Treat all sulphur-containing refinery fuel gas (RFG) in amine scrubbers to remove sulphur prior to burning;
- 2. Monitor the sulphur content of RFG and report it as an average over a suitable time period, e.g. monthly;

### Utilities

- 3. Set an appropriate target sulphur content limit, with the aim of moving towards the achievable level given in Annex 1 (Emission benchmarks);
- 4. After maximising the use of gas, use high efficiency heater designs with good control systems (e.g. oxygen trim), fitted with low or ultra-low NOx burners;
- 5. Use two or more control techniques to achieve reductions in NOx releases from 25 to 70% over conventional burners.

#### Flares

**Air:** releases to air are products of combustion or incomplete combustion and emissions from sour water from flare knock out pots and water seals when sour gas is flared in an emergency. **Water:** releases into water are of hydrocarbons, sulphur and nitrogen compounds from water drain, knock-out vessels and water seals.

**Odour:** hydrogen sulphide and other gaseous sulphur compounds can give rise to odour releases during sour gas flaring.

#### **Indicative BAT**

You should, where appropriate:

- 1. Use flaring as a safety system (start-up, shutdowns & emergencies);
- 2. Use a flare control system with a response sufficiently fast to avoid unnecessarily leaving steam injection running in order to anticipate flaring events;
- 3. Ensure smokeless and reliable operation;
- 4. Minimise flaring by a suitable combination of:
  - management information systems and instrumentation
  - balancing the refinery fuel gas system
  - installing a gas recovery system
  - using high-integrity relief valves
  - applying advanced process control.
- 5. Reduce relief gas to flare by management/good housekeeping practices.

### Utilities

#### Aqueous effluent treatment

**Air:** releases into air are of hydrocarbons evaporated from exposed surfaces.

**Water:** releases into water consist of the residual substances contained in the effluent after treatment. Depending on the nature of the refinery and the treatment efficiency these include hydrocarbons (dissolved and suspended), organic compounds (notably phenols), sulphur compounds (notably sulphides), ammonia/ammoniacal compounds and their derivatives after treatment. Traces of heavy metals are also likely to be present, arising from the desalting of crude oil feedstock and from caustic soda if this

contains trace contaminants, notably mercury.

Land: solid wastes comprise of wet sludges containing hydrocarbons deriving from the separation processes described above. The largest quantities typically arise from the primary and secondary treatment stages. Primary sludge deposited in the inlet chambers of API or plate separators may contain up to 10% oil and secondary sludge obtained from a flotation process may contain up to 30% oil. Excess activated sludge derived from biological treatment is typically much smaller in quantity and contains less than 0.5% oil. Complex refineries may produce much more sludge than simple refineries.

# 3 Emissions and monitoring

- 3.1 Emissions to water
- 3.2 Emissions to groundwater
- 3.3 Emissions to atmosphere
- 3.4 Abatement of nitrogen oxide emissions
- 3.5 Sulphur dioxide abatement
- 3.6 Abatement of particulate matter emissions
- 3.7 General controls
- 3.8 Fugitive emissions to air
- 3.9 Monitoring

### 3. Emissions and monitoring

### 3.1 Emissions to water

Water is used intensively as process water and for cooling. As a result, it becomes contaminated with oil products which increases the oxygen demand of the effluent. The main sources of waste water from a refinery are:

- process waters, arising from the refinery processes, typically as continual flows from specific plant items and including tank drainings, aqueous condensates (mainly via sour water strippers), purge streams, blowdown waters, coking process quenching and drilling waters, desalter underflows and process area drainage
- site drainage waters, running off hard surfaced areas that may be contaminated; both storm and firefighting cases need to be considered
- waste chemical solutions, arising from some refinery processes and utilities, including spent caustic solutions from sweetening units, effluents from

chemical treatment units, water treatment plant backwash, cooling system and boiler blowdown waters

- ballast waters, arising on some refineries which incorporate loading of product tanker vessels
- returned cooling water where "oncethrough" systems are used instead of recirculation and steam condensate where not re-used.

Oil and hydrocarbons are the main pollutants. Other pollutants are hydrogen sulphide, ammonia, phenols, benzene, cyanides and suspended solids containing metals and inorganic compounds (e.g. halides, sulphates, phosphates, sulphides). The following table summarises the main sources of water pollutants

Water Pollutant	Source
Oil	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain)
H <sub>2</sub> S (RSH)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic
NH <sub>3</sub> (NH <sub>4</sub> +)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, sanitary/domestic

### Main water pollutants emitted by refineries and their sources

Phenols	Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water
Organic chemicals (BOD, COD, TOC)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary/domestic
CN- (CNS-)	Visbreaker, catalytic cracking, spent caustic, ballast water
Total suspended solids	Distillation units, visbreaker, catalytic cracking, spent caustic, ballast water, sanitary/domestic
Heavy metals	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water

Effluent treatment removes for recycling as much of the oil as possible. Treatment processes fall into three main categories:

- primary, i.e. simple separation of gross oil and solids content, using techniques such as gravity separation, plate interception and tank interception
- secondary, i.e. more advanced separation of oil and solids content, using techniques such as flocculation, air flotation, sedimentation and filtration
- tertiary, i.e. treatment of residual and dissolved pollutants, using techniques such as biological processes, aeration and final polishing.

All refineries in England and Wales use primary treatment processes and increasingly secondary and/or tertiary processes to improve final effluent quality. The complexity of each refinery affects the composition of the effluent. Complete complex refineries require a greater extent of treatment than the simpler ones.

### Primary treatment processes

American Petroleum Institute (API) separator - a simple gravity separator that separates the more buoyant oil particles and settleable solids from the aqueous phase. Inputs to the separators may contain several per cent of oil. They remove all oil globules larger than 150microns and produce an effluent containing 50-100mg/l oil. Separation is achieved by a system of weirs, skimmers and scrapers; API separators typically form the initial treatment plant on most refineries. Other configurations are available to achieve the same separation, including tank separators with fixed skimming outlets.

*Plate separators* - a series of compactly arranged inclined plates, which the oil

particles coalesce against, become buoyant and rise to the surface to be skimmed off and re-cycled. Globules above 50 microns can be removed and effluent oil content is 30-50mg/I. They include the parallel plate interceptor (PPI) and the corrugated plate interceptor (CPI).

### Secondary treatment processes

*Flocculation/coagulation* – addition of a polyelectrolyte to flocculate and coagulate small oil globules and aid separation. It is continuously premixed into a dilute wetted form, then metered into the effluent at a controlled rate.

*Dissolved air flotation units* - Air is dissolved into water under pressure (up to 500kPa) and then released via ports into the separator. The resulting air bubbles become attached to the oil particles, increasing their buoyancy and causing them to float. The oil particles are then skimmed off intermittently and automatically for re-cycling.

Induced air flotation units - agitators mix the effluent with air as it flows through a series of chambers causing the oil particles to become buoyant as before. The oil is floated off continuously. The unit can be enclosed so minimising hydrocarbon losses. Both techniques remove suspended solids as well as oil particles. Oil levels in effluent can be reduced to 30 mg/l or less, depending on the soluble oil/hydrocarbon content of the effluent.

*Filtration techniques* – sand filters are also used. Units run in parallel either on-line or being back-flushed to collect the deposited solids as a sludge.

### Tertiary treatment processes

Biological treatment - Aerobic type biological treatment is very effective at breaking down organic compounds and other dissolved pollutants in most refinery effluents and reducing the final BOD and COD to acceptable levels. Most of the phenols, sulphides, other organics and ammonia are destroyed. Acclimatised biomass (mainly bacteria), in an appropriate medium, digests and oxidises many organic/nitrogen-containing compounds. Available processes include activated sludge units, aerated lagoons, trickle filters, and bio discs. Phenols and sulphides can be reduced to 1 mg/l or less with 80-90% reductions in COD and BOD. The biomass needs sufficient nitrogen and phosphorus to work efficiently. Nitrogen is available from stripped sour waters and phosphorus will normally is added. Air or oxygen is supplied to maintain aerobic conditions. Careful managing of the effluent-producing processes and balancing the pollutant load in the treatment plant is necessary to avoid shocks to the biomass.

Anaerobic type denitrification treatment is also used successfully on some refinery effluents where the nitrogen/carbon ratio is high enough for the biomass to use nitrate-derived oxygen to digest the organic constituents.

Sedimentation/filtration - treated effluent travels slowly through sedimentation tanks or ponds, followed if necessary by filtration using sand or gravel media filter. The settled solids are collected; part of the activated sludge is re-cycled to maintain the necessary biomass to effluent ratio and the remainder is de-watered and disposed of.

Scavenging/polishing - Scavenging with coagulants such as ferric hydroxide (from ferric chloride and sodium hydroxide) can be used to remove final traces of oil and suspended solids. The scavenged effluent is filtered through a media filter. After clarifying the supernatant final effluent, less than 3mg/l oil remains.

### General points relating to emissions to water

Refinery drainage systems, including effluent treatment must operate safely and efficiently at all times. Hydraulic flow must be maintained and avoiding dangerous concentrations of hydrocarbon vapours. which could cause a fire. The systems usually consist of pipes or channels with vented manholes and firetraps at regular intervals to keep the system flooded. There may be 40 or 50 manholes between a source of effluent and the first separator. Bulk hydrocarbons will tend to collect in the manholes as a lighter layer above the aqueous effluent and may remain static unless disturbed, e.g. by peak flow conditions.

Hydraulic design of systems allows for exceptional flow conditions including surge ponds and tanks or splitter boxes that allow excess storm/fire flow in parallel through separators normally in series. On some refineries, effluents are locally combined with returning "once-through" cooling water flows before entering the drains.

### **Indicative BAT**

#### Natural gas refining

- 1. Consider the following techniques in sequence to control releases to water:
  - minimise the quantity and contamination level of formation water to be treated onshore and control it at source "at source", ie off-shore. Measures include off-shore drying, minimising the use of dehydrating agents, using low toxicity corrosion inhibitors and improved field management, e.g. preventing "shock" pollutant loads arriving on-shore
  - use a three phase separator on the liquids from the slug catcher to control and minimise hydrocarbon content of the aqueous phase
  - treat sour condensate in a sour water stripper first
  - separate process effluent from glycol or methanol regeneration plants and any other high BOD/COD effluents from other streams, e.g. surface water, and treated before discharge to the site effluent system.

#### **Effluent treatment**

- 2. Observe and control effluent treatment plants from production control rooms;
- 3. Maintain API and plate separator units to a high standard:
  - plate packs should be kept clean / undamaged
    - level control/oil skimming systems should be frequently checked and adjusted to
      operate as designed.
- 4. Improve the performance of separators and reduce water loads on recovery plants by using advanced skimming techniques such as disc-type devices. Low shear pumps should be used to deliver effluent collected in the main inlet sump to the primary separator to avoid oil globule break -up and emulsion formation, with subsequent flow through the plant by gravity
- Include arrangements to adjust the pH by appropriate acid or alkali additions to lie between 7 and about 8.5 to maintain optimum biomass conditions. Facilities to add alkali to correct acid pH should be provided to deal with acidic excursions
- 6. Provide pollutant balancing
- 7. Separate "once-through" cooling water from any effluent streams containing significant amounts of suspended or dissolved pollutants in order that these may be treated as appropriate, unless you can demonstrate that this will give no environmental benefit. Continuing to rely on this cooling method for existing refineries can only be justified if you take due care to prevent oil or other hydrocarbons being in returned cooling water. Appropriate measures include high grade cooling tube/plate materials to avoid corrosion failures, adequate preventative maintenance and effective monitoring for the presence of oil in cooling water returns with immediate action if it is detected.

- 8. Minimise releases of VOCs to air from effluent systems by keeping the light hydrocarbon content of waste waters to a minimum and by covering as much of the ETP as possible, especially the primary and secondary units which contain the most free hydrocarbons.
- 9. Install fully developed treatment (primary + secondary + tertiary) for complete or partial complex refineries, with tertiary stage BAT being a biological treatment process. Fully developed treatment may also be BAT on simple refineries, but this will depend on circumstances and primary + secondary treatment may be acceptable in some cases.

#### Bunds

- 10 Ensure that areas where spillages are most likely, including any pig receiving facilities on pipelines, process plants, storage tanks, sampling and loading points, are bunded or kerbed and drain to sumps from which oily sludges, spillages etc can be removed, preferably to recovery plants. The composition of any wastes collected should be checked prior to treatment or disposal;
- 11 Bund floors and walls should be impermeable to water and to the materials in tanks and pipelines within the bund.
- 12. Fit high level probes and alarms to bunds that are not frequently inspected, based on a risk analysis;
- 13. Recycle recovered oil by steam heating it to break down oil/water emulsions. The aqueous phase should be returned to treatment while the hydrocarbons should be recycled or used as fuel for heaters or furnaces;
- 14. Not use pipelines, vessels or tanks that have leaked into a bund until they have been repaired;
- 15. Note that mineral oils and hydrocarbons are List 1 substances controlled under the Groundwater Regulations 1998 and must be prevented from entering groundwater. The design, operational management and performance, maintenance, inspection and repair of bunds as a key issue in meeting this requirement.
- 16. Check the composition of any wastes collected prior to treatment or disposal. Wastes containing more than 0.1% oil are hazardous wastes according to the European Waste Catalogue. Rainwater collected from oil tank bunds should be discharged via an oil separator. Water from bunds of tanks containing other chemicals should not be disposed of via surface water drains or soakaways.
- 17. Ensure that existing earth and clay bunds are fit for purpose. A thorough review of earthclay bunds is required. This should include:
  - bund and storage / process vessel / pipelines capacities
  - bund wall design and construction (including thickness of engineered clay layer), strength, resistance to water-logging
  - potential for slop-over in event of tank failure

- floor design and construction (e.g. confirmation of clay/impervious layer thickness and that it is compressed and not natural clay subject to fissures), strength and stability
- hazardous waste removal (e.g. contaminated soils following loss of containment incidents within bunds)
- design and operational arrangement for bund isolation and necessary regular drainage management of bunds
- confirmation that bund contents can not be in hydrological contact with groundwater.

#### Drainage including rainwater

- 18. Contain and treat site drainage waters (including rainwater) from bunded or hard surfaced areas, and emergency fire water before release. They may have been contaminated with hydrocarbons and should be kept separate from clean storm water drainage and treated in an oily water treatment plant. The separated oil should be skimmed off and re-cycled to the process or removed to an oil recovery/treatment facility;
- 19. Provide storm/fire surge containment including arrangements to overflow or pump to surge facilities, from which contaminated water can be returned for subsequent treatment. Drains containing potential pollutants should be located in suitable pipe trenches so that any leaks may be contained, observed and repaired quickly;
- 20. Discharge treated drainage waters from small sites to a ditch, soakaway or other suitable watercourse but in some circumstances (eg on complex sites with large hard surfaced catchment areas) it may be preferable to re-inject into the oilfield for all but the severest storm event;

#### Tankage

21. Bund oil storage tanks and fit them with high level alarms and pump cut-outs to avoid spillage. Remote well sites that are normally unmanned should preferably transmit tank level data, including alarm conditions, to a manned site. Tanks should have level gauges visible from the filling point. Pipework should preferably be overground. Where it must be underground it should be protected in a sleeve or a duct;

#### Oil slops recovery

22. Provide oil slops recovery at gathering centres to facilitate oil re-cycle to process from the centre itself and from remote well sites. Bulk separation of oil and water is carried out in a heated tank. The oil is transferred to the incoming receipt tank and the oily water is treated, as above;

#### Radionuclides

23. Inform us immediately whenever naturally occurring radionuclides are encountered Reconsider operations so as to minimise the amounts and activity of contaminated materials. Application for authorisation under the Radioactive Substances Act 1993 may be necessary if radioactive waste is being accumulated and/or disposed;

24. Investigate the source(s) and destination(s) of radionuclides and consider any appropriate changes to operations, particularly to the well fluid and produced water systems. Techniques have been developed that can inhibit scale deposition on equipment, trap the contamination on inserted surfaces that have a preferential affinity for the radionuclides concerned (including ion-exchange resins) and flush contaminated waxy solids through prior to plant shut-downs;

#### **Materials handling**

- 25. Store liquid feedstocks in roofed tanks enclosed in bunded areas capable of holding 110% of the tanks contents. Where oil is being handled the area should be hard surfaced and slope towards a drain leading to an interceptor with facilities for the removal of the oil. All oil storage areas should include adequate precautions to prevent oil reaching drains leading directly to controlled waters;
- 26. Drain decanted water from oil storage tanks, storm water from bunded areas and liquid effluents generated from tank cleaning to a water treatment plant, or direct to an appropriate disposal facility. Oil contaminated water should pass through oil removal facilities such as partition chambers or plate separators;
- 27. Recycle and re-use water from handling coal suspensions. Any coal sludge produced by separating water and coal should be re-cycled into the gasifier feed;

#### Process liquors/other wastes

- 28. Treat process waters. Where aqueous quenching is used, separate the quench product into aqueous and non-aqueous phases. Recirculate the aqueous phase and send the purge stream to the effluent treatment plant
- 29. Re-inject tars, oils and associated particulate matter into the gasifier;
- 30. Neutralise and/or settle and biologically treat minor waste liquors from gasification processes;
- 31. Chemically treat, neutralise and settle effluent from wet scrubbing before discharge. Acidity is adjusted by adding lime or other alkali. Heavy metals may be removed by precipitation and solids separation. Activated carbon removes mercury. Organics should be quantified in the treated effluent. At low levels they are normally most effectively treated in a biological plant, normally by the Sewerage Undertaker;

#### **Cleaning liquids**

- 32. Neutralise and treat wash waters and cleaning-out solutions containing organic acids, alkalis, alkali phosphates, iron oxides in suspension, complex corrosion inhibitors or acids;
- Consider off-site treatment for water contaminated with detergents and/or solvents from off-line turbine washing;

#### **Cooling tower purge**

- 34. Minimise the use of biocides in evaporative cooling towers by optimising the dosing regime, (e.g. intermittent shock dosing or only dosing at critical times of the year). Using automatic mechanical cleaning systems for main condensers, limits chemical control to auxiliary systems. The biocide system should prevent accidental overdoses of biocide being released to the environment. This involves monitoring of levels in the outgoing water and automatic operation of the final discharge valves, as well as bunding of storage vessels and adequate procedures;
- 35. Ensure that specifications for treated timber include the requirement for controlled washing at the treatment site. Timber used in cooling towers is usually treated with CCA (copper sulphate, potassium dichromate, arsenic pentoxide), most of which remains well bound to the timber over its operating life, but initial surface residues can lead to significant levels in the purge water;

#### Waste water treatment

36. Consider the use of filtration/osmosis or other techniques which allow the Effluent water to be cleaned for release or returned to the process. The concentrated residues of such techniques should be returned to furnaces, evaporated, solidified or sent for incineration. If the pollutants in the wastewater are all readily biodegradable or the effluent contains only materials which are naturally occurring in much larger quantities in the receiving water, there may be justification for filtration/osmosis or similar techniques not being considered appropriate;

#### Water treatment/de-ionisation effluents

37. Ensure that all water treatment/de-ionisation effluents are well mixed and neutralised before discharge. This effluent contains dissolved and undissolved solids and soluble sulphates and the presence of salts in the release should be considered.

## **Emissions to groundwater**

### 3.2 Emissions to groundwater

Potential releases to water from on-shore oil processes consist of produced waters separated from well fluids and site drainage waters running off bunded or hard surfaced areas that may be contaminated. Produced waters mainly arise at the phase separators, but smaller quantities also occur from tank drains, process blow-down sumps and from the pigging of pipelines. They are saline and normally contain free and emulsified hydrocarbons as well as dissolved or suspended solids. They should not be discharged to surface water or soakaway. In some fields the suspended solids may include low concentrations of naturally occurring radionuclides.

Produced water is disposed of by reinjecting into the oilfield, either to a producing formation as part of the disposal well. Small quantities of produced water may be disposed of off-site where re-injection is not justifiable. Where reinjection is to a producing formation the water should be treated as part of normal oilfield management, particularly to prevent bacterial souring of the reservoir (by biocide addition) or the hydraulic blocking of porous rock strata with solid particles (by filtration/settling). Reinjection is a release to ground, i.e. controlled waters, and that any conditions required to protect ground waters should be included in the authorisation for the process; these may be particularly stringent for sites located in important or vulnerable aquifer areas. Re-injection may be unacceptable in some circumstances, e.g. highly fractured geology, and off-site disposal may then be required.

reservoir pressurising system or to a

### Indicative BAT

You should, where appropriate:

- 1. Re-inject produced water into the same oilfield, either to a producing formation as part of the reservoir pressurising system or to a disposal well. Re-injection should be made below the oil-bearing strata via dedicated wells, and any conditions required to protect ground waters should be included in the authorisation for the process;
- 2. Treat the produced water prior to re-injection by degassing and separating from entrained oil prior to passing to bunded holding tanks and adding biocide. The biocide(s) used should not contain any substance prescribed for release to controlled waters in Schedule 5 of the Regulations. The cumulative discharge of produced water should at no time exceed the cumulative fluid withdrawal from the reservoir.

### **Emissions to atmosphere**

### **3.3 Emissions to Atmosphere**

The main polluting substances released to air by refineries, on shore oil fields, and gas processing plants are:

- sulphur dioxide (SO<sub>2</sub>) and other sulphur compounds
- oxides of nitrogen (NOx) and other nitrogen compounds
- carbon monoxide (CO)
- volatile organic compounds (VOC), in particular hydrocarbons
- particulate matter (PM), including metals and their compounds; and carbon dioxide.

Power plants, boilers, heaters and catalytic cracking are the main sources of emissions of carbon monoxide and dioxide, nitrogen oxides (NOx), particulates, and sulphur oxides (SOx) to the atmosphere. Typically more than 60 % of refinery air emissions are related to the production of energy for the various processes. Sulphur recovery units and flares also contribute to those emissions. Catalyst changeovers and cokers release particulates. Volatile organic compounds (VOCs) are released from storage, product loading and handling facilities, oil/water separation systems and, as fugitive emissions, from flanges, valves, seals and drains. Other emissions to the atmosphere are H<sub>2</sub>S, NH<sub>3</sub>, BTX, carbon disulphide (CS<sub>2</sub>), carbonyl sulphide (COS), HF and metals as constituents of the particulates (V,Ni and others). The following table summarises the main pollutants emitted by a refinery, with their main sources.

Main air Pollutants	Main sources
Carbon dioxide	Process furnaces, boilers, gas turbines, fluidised catalytic cracking
	regenerators, CO boilers, hydrogen plant, flare systems, incinerators
Carbon monoxide	Process furnaces and boilers, fluidised catalytic cracking regenerators, CO boilers, sulphur recovery units, flare systems, incinerators
Nitrogen oxides (N <sub>2</sub> O, NO. NO <sub>2</sub> )	Process furnaces, boilers, gas turbines, fluidised catalytic cracking regenerators, CO boilers, coke calciners, incinerators, flare systems

### Main air pollutants emitted by refineries and their sources

### **Emissions to atmosphere**

Particulates (including metals)	Process furnaces and boilers (particularly when firing liquid refinery fuels), fluidised catalytic cracking regenerators, CO boilers, coke plants, incinerators
Sulphur oxides	Process furnaces, boilers, gas turbines, fluidised catalytic cracking regenerators, CO boilers, coke calciners, sulphur recovery units (SRU), flare systems, incinerators
Volatile organic compounds (VOCs)	Storage and handling facilities, gas separation units, oil/water separation systems, fugitive emissions (valves, flanges, etc.), vents & flare systems
Benzene	See VOCs
Polycyclic Aromatic Hydrocarbons (PAHs)	See VOCs

The main source of CO<sub>2</sub> emissions is from energy production. Refinery energy demand has increased as product specifications get tighter and a shift over the years from producing heavy fuel oils to transport fuels.

Carbon monoxide (CO) is an intermediate product of the combustion processes particularly in sub stoichiometric combustion conditions. CO releases from refineries are not very high compared to CO<sub>2</sub>.

Particulate emissions result from the combustion of fuel oils, especially when there is sub-optimal combustion. When included in a refinery configuration the catalytic cracker is the largest individual source of particulates. Particulate emissions are often associated with metal releases.

VOC emissions arise from the evaporation and leakage of hydrocarbon fractions during storage and distribution. Hydrocarbons may also be emitted during non-optimal combustion conditions. Volatile organic carbons (VOC) include benzene and other aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). The main sources of benzene in the atmosphere are the petroleum and petrochemical industries and other combustion processes. PAHs are generated when organic matter, including fuels, is combusted. Coal-tar pitch volatiles (CTPVs), which contain PAHs, are produced during coking, tar distillation,

### **Emissions to atmosphere**

aluminium smelting and downstream uses of tar and pitch.

Oil refineries are highly significant energy users. Many installations will have combustion plants providing both steam supplies and process heating. Combustion plants that have a thermal input 50 MW or more (maximum continuous fuel rating) are subject to the Large Combustion Plant Directive (see Annex 1 of "*Getting the basics right*"). New gas turbines are subject to the Directive. With respect to oil refineries, the Directive does not apply to:

- facilities for the regeneration of catalytic cracking catalysts, and
- facilities for the conversion of hydrogen sulphide into sulphur.

Refineries use both refinery fuel oils (RFO) and refinery fuel gas (RFG). RFG is a low sulphur fuel, as its sulphur content is normally below 100 ppm. RFO has a variable sulphur content. Oil refineries have a derogation under the Sulphur in Liquid Fuels Directive (see Annex 2) which means they can burn RFO with a sulphur content greater than 1% in some combustion plants, provided that the flue gas sulphur dioxide concentration averaged across the refinery is less than 1700 mg/m3.

The sulphur content of RFO depends on the slate (the spread of feedstock crude

oils) fed into the refinery operations and the processes operated. Most UK refiners operate a fluidised catalytic cracker and they produce gas fractions, which increase the availability of RFG.

Where a refiner is burning the maximum amount of RFG available, any further energy requirement means that SO<sub>2</sub> releases will rise because more RFO is burnt to meet the extra demand.

Abatement of SO<sub>2</sub>, NOx and particulates can be applied in three main areas:

- upstream abatement by ensuring the fuel is as 'clean' as possible, i.e. burning low sulphur refinery gas or natural gas rather than heavy fuel oil reduces the SO<sub>2</sub>, NOx and particulate releases;
- using abatement inside a boiler, furnace or reactor in which combustion or a chemical reaction is taking place and ensuring combustion is as complete as possible;
- abating releases downstream of combustion plant or reactors.

Burning clean gaseous fuel will normally provide significant improvement in SO<sub>2</sub>, NOx, particulates, heavy metals and CO<sub>2</sub> compared to the combustion of the equivalent amount of heavy fuel oil. During the crude oil refining process, sulphur and

# Abatement of nitrogen oxide emissions

other potential pollutants tend to be concentrated in the heavier, lower value fractions and products.

There are various well established processes for the removal of sulphur from liquid fuels (see section on sulphur dioxide abatement). Heavy fuel oil can also be converted to "clean" gaseous fuel by gasification. This can be applied to a wide range of low-value oil products including:

- residual oils including vacuum residue, asphalt/pitch
- petroleum/water emulsion including orimulsion; and
- petroleum coke.

The resulting products are virtually sulphur-free and have increased value. The clean gas can be fired in furnaces or gas turbines, and used for production of hydrogen or in the synthesis of a range of liquid fuels and chemicals. The gasification unit also produces export steam.

### 3.4 Abatement of nitrogen oxide emissions

#### General

Nitrogen oxides (NOx) come from combustion processes. During the combustion of fuel, nitrogen (from the combustion air) is transformed to a mixture of NO<sub>2</sub> and NO. Levels of NOx released depend on many factors including combustion temperature and oxygen concentration (thermal NOx) and the amount of nitrogen in the fuel (fuel NOx). High hydrogen in the fuel results in higher flame temperatures and higher NOx formation.

Fuel NOx can range from non-existent in the case of natural gas to several times the thermal NOx for certain residue fuel oils. Coke deposits on catalyst, applicable to FCCUs, can also be high in nitrogen. The proportions of total NOx emission from various types of equipment on refineries are typically as follows:

Combustion plant	80%
FCC units	15%
Other units such as	5%
calciners, flares, etc	

Combustion of fuel oil tends to produce 3 to 5 times the amount of NOx compared to the combustion of the equivalent amount of gas. Firing low NOx burners with fuel oil containing 0.3wt% nitrogen will typically produce about 450mg/Nm<sup>3</sup> of NOx (thermal and fuel).

Low NOx residual oil burners cannot achieve similar release levels to low NOx gas burners. The amount of NOx a refinery releases depends on the proportion of fuel oil to fuel gas that is fired in the combustion plant. Typically this is 60% gas, 40% oil, but can be as high as

# Abatement of nitrogen oxide emissions

60% oil. Auto oil legislation has reduced the amount of fuel gas available on a refinery as the hydrogen is required for additional hydrotreatment to achieve reduced levels of sulphur in fuels.

#### Upstream abatement of NOx

Hydrotreatment (to remove sulphur compounds) removes 15-40% of nitrogen compounds. The nitrogen compounds, especially in residues used as fuel oil, increase the levels of NOx when the fuel is burnt. However, installing hydrotreatment purely for pollution abatement is expensive.

### In-furnace abatement of NOx

### Low NOx burners

30–40% reduction in NOx can be achieved by fitting conventional low NOx burners. Low NOx burners apply staged burning to achieve lean combustion which results in lower flame temperature and lower NOx levels. Low NOx burners designed for firing refinery gas typically achieve 100mg NOx/m3 at 3% excess oxygen. Low NOx (LN) burners fitted to some older furnaces and boilers are less effective. Retrofitting to oil-fired furnaces is generally less effective than to gas-fired furnaces.

New ultra low NOx (ULN) burners can achieve 80mg/m<sup>3</sup>.

Forced draught heaters can achieve 80 mg/m<sup>3</sup> with ULN burners when firing on refinery fuel gas. NOx increases if air preheat temperatures increase above 150°C, if the hydrogen content goes above 80%, or if firebox temperatures increase.

For natural gas firing with ULN burners in forced draught heaters, NOx emissions will typically be 100mg/m<sup>3</sup>. Again NOx will increase under the conditions described above.

Natural gas firing with ULN burners in forced or natural draught conditions may show signs of instability, particularly at low turndown and low excess air. ULN burners may not be suitable for some boiler designs.

### Other in-furnace NOx reduction techniques

Recirculating flue gas as part of the combustion air can reduce NOx formation but the process is difficult to control and to operate safely especially during turndown. Using recirculated flue gas is not considered appropriate for refineries, gas refining or on-shore oil production.

### Downstream flue gas abatement of NOx Selective catalytic reduction (SCR)

80 – 90% NOx can be removed by selective catalytic reduction (SCR). NOx is reduced to nitrogen and water using

# Abatement of nitrogen oxide emissions

ammonia over a catalyst. The ammonia is injected into the flue gas upstream of the catalyst. Some of the ammonia is not reacted and emerges with the flue gases. This is termed 'ammonia slip'. The catalytic reaction usually requires temperatures between 260 to 600°C to be effective. Location of the catalyst in the flue gas system is important and may restrict its application in some cases. Lower-temperature SCR processes which operate between 100 - 150oC are now available. Pressure drop is also important and the technique is not applicable to natural draught furnaces with low pressure drops.

### Selective non-catalytic reduction (SNCR)

Thermal NOx reduction, also called selective non-catalytic reduction (SNCR), is available. Ammonia is injected into combustion gases at temperatures of 870 to 1100°C. Temperature and residence time requirements can restrict the application of SNCR, and, as in SCR, ammonia slip occurs. It has been applied to FCCUs where a CO boiler provides a sufficient temperature window. It may be applicable to boiler systems but less so to fired heaters.

SNCR should be considered as BAT where a suitable temperature window and design of plant exists for its application. Typically SNCR can provide about a 50% reduction in NOx given a suitable temperature window.

### Indicative BAT

You should, where appropriate:

- 1. Use firing of gas with ultra low NOx burners associated with conventional forced and natural draft furnaces and boilers on oil refineries, gas refining and on-shore oil fields
- 2. Test the burners to explore the limits of combustion prior to site installation to ensure reliable operation
- 3. Minimise the firing of fuel oil. Where this occurs, low NOx burners should be used. In addition, where practicable, SCR should be considered on large oil-fired plant. Sticky sooty particles from the combustion of heavy fuel oil may necessitate arrestment equipment upstream of the SCR.

### Spark ignition reciprocating engines

There is a specific NOx problem with spark ignition reciprocating engines, which are often used on older existing refrigerant compressors and occasionally, in turbocharged form, on some product gas compressors. The low engine speeds and long residence time at high temperature,

leads to considerable thermal fixing of nitrogen from the combustion air. The small size engines cannot be modified or fitted with post-combustion NOx abatement. Best available techniques are converting to a nonrefrigerant dew-point process or replacing the compressor/engine. Using such engines as product gas compressors is not BAT. The use of abatement such as SCR should be considered.

### 3.5 Sulphur dioxide abatement

### General

Sulphur dioxide originates from a number of sources, including combustion processes, fluid catalytic cracking (FCC) units on refineries and sulphur recovery units (SRU). Proportions of total SO<sub>2</sub> emissions from various types of refinery process plant are typically as follows:

Combustion processes	50 to 60%
Fluid catalytic cracking units	15 to 20%
Sulphur recovery units	10 to 20%
Flaring and other releases	10 to 20%

### **Combustion processes**

Gas processing plants and oil field facilities normally burn exclusively gas from the fields that they are designed to process. SO<sub>2</sub> releases are lower than from oil refineries provided that hydrogen sulphide has been removed.

Most refineries adopt a dual fuel strategy. The resulting air emissions depend on the type and balance of fuels burnt, which are usually refinery fuel gas and fuel oil. Refinery fuel gas is the main fuel. Standby fuels are fuel oil or propane. Refinery fuel gas is normally much lower in sulphur than fuel oil and typically contains about 50% hydrogen. Increasing levels of hydrogen reduces the molecular weight of the fuel gas and increases its combustion temperature. Typically, refineries in the UK are burning refinery fuel gas with sulphur content, as  $H_2S$ , ranging from 0.05 to 0.6 vol% and fuel oil with a sulphur content of 0.8 to 4.5% by weight.

### Sulphur in refinery fuel oil

Low sulphur crude produces lower sulphur fuel oils on a refinery. The amount of sulphur in the fuel oil also depends on its source within the refinery. This is usually vacuum residue, the bottom flow from the vacuum distillation tower. 1.5% or better sulphur fuel oil can be produced from lowsulphur North Sea crude. Fuel oil can also be sourced from other points, including the

bottom flow from the atmospheric distillation column. Sulphur levels in the fuel oil can be reduced at some cost to the refiner by 'cutting back' with, for example, desulphurised gas oil.

Sulphur can be removed from refinery feed and product streams by hydrotreatment. Sulphur is converted to hydrogen sulphide under pressure and at elevated temperature in the presence of hydrogen over a catalyst. It is easier to remove from the lighter, lower boiling range, hydrocarbon streams as less hydrogen is required and a lower reactor pressure is needed, typically 30-40 bar. Hydrotreatment of a heavy high sulphur residue stream and hydrocracking, require pressures of the order of 50-80 bar and 80-200 bar respectively which are energyintensive. They also require more catalyst and more hydrogen than the hydrotreatment of lighter streams and are very expensive in investment and operating costs. The production of low sulphur fuel oil from high sulphur fuel oil is not economic. These energy-intensive procedures are not regarded as BAT for the production of low sulphur fuel oil, solely for combustion on refinery boilers and furnaces.

Hydrotreatment of heavy residues may be considered when there is a market for the product or where high sulphur fuel oil cannot legally be burnt. Refineries are able to burn higher sulphur fuel oils so long as  $SO_2$  emitted across all plants (excluding 'new' large combustion plants which fall under the scope of Directive 88/609/EC) does not exceed 1,700mg/m<sup>3</sup> (approximately equivalent to 1% sulphur fuel oil) as a monthly average, irrespective of the type of fuel or fuel combination used.

#### Sulphur in fuel gas

Fuel gas on refineries, oil fields and gas processing plants usually comes from a variety of sources, which are pooled in the fuel gas system. Sulphur content of the fuel gas depends on the sulphur content of the produced crude oil or gas. Sulphur content of the gas is usually reduced by scrubbing with amine solution, although other methods are available. The amine solution absorbs the hydrogen sulphide and is then regenerated by heating with steam. The resulting hydrogen sulphide is piped to a sulphur recovery unit.

Amine treatment units can achieve 100ppm levels or better. Some refineries are already achieving less than 100ppm sulphur in their fuel gas.

As the performance of amine treating is a function of partial pressure, resulting  $H_2S$  concentrations in fuel gas are generally quoted in molar or volume terms, so that with varying molecular weight of the gas, performance remains the same. The molecular weight will vary due mainly to the amount of hydrogen in the system.

### **Indicative BAT:**

 For reliable operation, amine systems need filtration to remove dirt and activated carbon treatment for hydrocarbon removal, otherwise foaming and other operating problems result with associated loss of performance.

### Reducing sulphur dioxide formation in the furnace

In certain furnace and firebox designs, lime or limestone can be injected to absorb the sulphur dioxide formed during combustion. In particular, fluidised bed or circulating fluid bed (CFBs) boilers, which are especially suitable for burning petroleum coke or heavy asphalts. 50 -60% reduction in SO<sub>2</sub> is possible using limestone slightly in excess of stoichiometric quantities. 80 - 90% reduction is possible with excess limestone. Existing boilers and furnaces on refineries, gas and oil field facilities are not normally suited for lime/limestone injection. Fluid bed or CFB boilers should be considered for future installations.

### Reduction of sulphur dioxide in the flue gases

Pressure drop is an important consideration in respect of downstream abatement, particularly in the case of natural draught furnaces. The capital cost of equipment for downstream SO<sub>2</sub> abatement on boilers, furnaces and FCCU regenerators largely depends on flue gas flowrates. Wet scrubbing of the flue gas from FCCU units is widely used, other scrubbing processes are less likely to be suitable for flue gas cleaning on refineries.

#### Wet gas scrubbing processes

 $SO_2$  is removed from the flue gas by reaction with an alkaline solution in a scrubber to produce a soluble sodium sulphate effluent and clean gas. The clean gas is emitted and the liquid is recycled to the contacting scrubber. There is a constant purge of slurry and corresponding make-up of solution. Up to 90% removal of  $SO_2/SO_3$  and particulates can be achieved. Nearly all  $CO_2$  can also be absorbed.

### Dry and semi-dry processes

 $SO_2$  is removed from the flue gas by reaction with lime using a spray drier in which the hot flue gas is contacted with a spray of fine droplets of lime slurry. The  $SO_2$  is absorbed into the droplets, which are dried to a fine powder by the hot flue gas. In the dry process, dry lime is injected into the flue gas as finely dispersed particles. Both dry and semi-dry processes require downstream dust arrestment systems, such as an electrostatic precipitator (ESP) or bag filtration. The dry process achieves about a 50% sulphur reduction. Dry and semi-

dry FGD systems have been extensively used in the power industry but not widely on refineries. They are probably not suitable for natural draught furnaces or FCCUs and compatibility may be doubtful on other refinery combustion plant.

#### Other SO<sub>2</sub> removal processes

Other SO<sub>2</sub> removal processes are possible, but have not been widely applied to refineries. They include:

Limestone gypsum (including semi-dry process). Widely applied in the power industry on large electrical generating stations but less applicable to the refinery industry due to the amount of solids handling required and the smaller flue gas flows;

Sea water scrubbing. The natural alkalinity of the seawater can remove up to 90%

SO<sub>2</sub>. Large volumes of water are used in the process. The environmental effects of the acidic process effluent on estuarine waters would need thorough assessment.

*Dry catalytic process.* Removal of  $SO_2$  is by absorption on and reaction with metal oxides held in a matrix in a reactor vessel.

Overall, the costs of installing SO<sub>2</sub> abatement equipment to flue gas streams on boilers and furnaces on refinery, gas plants and oil field facilities will exceed measures that can be adopted to reduce the sulphur in fuels and achieve a similar level of abatement. SO<sub>2</sub> scrubbing may be appropriate where a number of larger emitters feed to a single stack. Combustion of clean low sulphur fuels is considered BAT, especially on existing refineries with a number of individual flue gas stacks.

### **Indicative BAT**

You should, where appropriate:

- 1. Use fuels which contain 1% by weight of sulphur, or better, in fuel oil and 100ppm vol/vol or better of H<sub>2</sub>S in the fuel gas;
- 2. Be able to demonstrate that all appropriate methods for reducing sulphur in fuel have been thoroughly evaluated;
- 3. Select clean gas for combustion throughout the plant;
- 4. Use amine treatment of all significant sour gas streams to a level of 100ppm vol/vol of H<sub>2</sub>S or better;
- 5. Be able to demonstrate that fuel selection has been thoroughly evaluated.

# Abatement of particulate matter emissions

### **3.6 Abatement of particulate matter emissions**

Particulate loads from refinery combustion plant are normally low except when heavy fuel oil residues are burned. Particulate loads can be high from FCCU regenerators. As gas refining and onshore oil field facilities normally burn gas, particulate releases from combustion on these facilities are normally not significant.

Abatement techniques for combustion includes cyclones, electrostatic precipitators (EPs), and wet scrubbing. Cyclones remove larger particles but not the smaller ones especially PM10 and below. They can provide significant particulate removal in combination with other types of abatement plant.

Bag filters are not favoured for most refinery processes due to their pressure drop, the potential for 'blinding' if the particles are 'sticky', the large space needed, temperature limitations and performance in upset conditions. Natural draught furnaces and FCCUs are particularly sensitive to pressure drop changes. Bag filters are more suitable for particulate abatement at moderate temperatures downstream of a waste heat boiler on a coke/calciner unit. Wet scrubbing can remove up to 95% of particles as well as  $SO_2$  on FCCUs.

Electrostatic precipitators (EPs) are installed on some refinery plant, especially FCCUs in the USA. In combination with upstream cyclones, EPs can achieve below 50mg/m<sup>3</sup> particulates. Particulate removal by EPs from FCCU flue gas may be reduced due to the high and varying resistivity of the catalyst dust or when operating on very low sulphur flue gas levels. Ceramic filters on cyclone underflow systems will also achieve about a 50mg/m<sup>3</sup> release. Ceramic filters designed to filter the complete gas stream have not yet been installed on refinery FCCUs.

# Slags, ash and other particulate matter from gasification /gas purification and conversion

Processes utilising solid feedstock will produce large quantities of slag or ash from the gasifier bottom. These solid wastes may be saleable or acceptable at a licensed waste disposal site.

Fly slag or ash will also be recovered from the purification train. In some cases the fly material may still contain significant proportions of ungasified carbon/organics. Liquid feedstocks may produce some particulate matter, which will be collected in the purification sections. Depending on their composition, these materials may be

## **General controls**

re-cycled to the gasification process or disposed of to a licensed waste disposal site.

Oil or oil emulsion fed gasifiers will release soot and ash, which contain heavy metals, particularly vanadium. This material requires special handling and may not be recyclable. Vanadium recovery processes are available. Soot and ash carried out of the gasifier with the product gas are scrubbed out in an aqueous slurry. The soot and ash are filtered out of the slurry. The filter cake is then dried and burnt under controlled conditions to produce an ash. The ash components are recovered as oxides, for example vanadium pentoxide, which may then be sent for use in the metallurgical industry. Other metals such as nickel should be recovered, where possible. These metal recovery processes represent the BAT for these waste streams.

### **Indicative BAT**

You should, where appropriate:

- 1. Use wet scrubbing technology where sulphur dioxide and particulates releases are high and both require abatement. For example, large furnaces and boilers combusting high sulphur heavy fuel oils and to FCCUs with high sulphur feedstock;
- 2. Use cyclones followed by an electrostatic precipitator for furnaces, boilers and FCCUs where particulates only are required to be abated. An EP may be sufficient without associated cyclones for furnaces and boilers, but you must be able to justify your choice;
- 3. Recover metals, e.g. vanadium and nickel from ash and soot, from particulate waste streams.

### **3.7 General controls**

### Volatile organic compounds (VOCs) releases

VOC releases should be minimised from refinery utility and ancillary systems and during plant maintenance and cleaning operations. Hydrocarbons should be minimised in cooling water and adequate separation facilities provided to deal with contamination. After depressurising offline process vessels to RFG/flare, they should normally be steamed out to flare and residual liquids returned to oil slops plants, not run to drain before venting to air, when people need to enter.

### **Relief valve releases**

Typically relief valves vent either to atmosphere or to a closed relief system leading to a flare (ground or elevated). With time, relief valves tend to leak and generally leak once called into operation.

# **General controls**

Several older refineries relieve either a portion to flare or the total to atmosphere.

### Storage/loading/unloading

Loading, unloading and storage of hydrocarbons can give rise to significant releases of VOCs.

### Pigging activities and depressurisation – vapour recovery

Launching and receiving pigs associated with oil and gas pipelines requires the pig launchers and receivers to be opened to the atmosphere when inserting or withdrawing the pigs. The pig receiver must be depressurised before opening. Other plant and equipment on refineries, gas refining plant and on-shore oil fields may also require periodic depressurisation and venting. Depressurisation gives rise to venting of hydrocarbon vapours and perhaps liquids.

### Vessel cleaning/steam-out

It is standard practice, particularly on oil refineries, to steam out vessels to remove hydrocarbons before people enter the vessel. Steaming out can give rise to significant VOC release to atmosphere.

### Hydrocarbons from miscellaneous sources

The small quantities of hydrocarbon vapours derived from produced water degassing, glycol regeneration and

hydrocarbon drains should be directed to flare. The following should be used to treat VOC emissions that are remote from the RFG system:

- condensation, e.g. using direct/indirect refrigeration at -40°C or below
- condensation using liquid nitrogen spraying
- carbon bed adsorption with vacuum regeneration and liquid absorption
- membrane vapour enrichment with pressure swing adsorption
- direct cold liquid absorption.

Details may be found in Environment Agency guidance note A2.

Thermal incinerators should operate at an appropriate temperature and residence time at temperature to achieve a high destruction efficiency with adequate mixing in the combustion zone. Catalytic incinerators or flameless thermal oxidisers can typically achieve the same or better destruction efficiency at a lower temperature. With incineration, the use of flame/detonation traps or other safeguards is essential.

### Refrigeration systems

Refrigerants that are of significant environmental concern, which will escape during operation, should not be used. Hydrocarbons such as propane or butane are considered the best available technique. Refrigeration systems should be subject to LDAR programmes.

## **General controls**

Alternative non-refrigerant techniques should be considered for dew-point control, ie molecular sieve or silica gel systems; they are likely to have cost and environmental advantages in most cases.

### **Carbon dioxide**

Acid gas streams containing carbon dioxide free from sulphur and hydrocarbon compounds may be vented directly to air, although this may require heating to aid dispersion. Alternatives to direct release should be considered particularly for large carbon dioxide flows. If the stream has significant hydrocarbon content, it may be used in a suitable combustion process, e.g. mixed into site fuel gas or used on a utility designed to burn gas of low flame stability. Other alternatives include injection into fields in production or worked-out or commercial sale.

### **Indicative BAT**

You should, where appropriate:

### **Relief valve releases**

1. Test relief values on a regular basis, to check for correct operation. Where practicable, relief values that can give rise to VOC releases should be connected to a vent gas system to allow the VOCs to be collected and either recovered or flared;

### Storage/ loading/ unloading

- 2. Follow the requirements in "*Getting the basics right*" for the design of storage tanks and associated tank seals;
- 3. Install vapour recovery at loading and unloading points from road, rail and ships. In particular where the hydrocarbons being handled have a high vapour pressure. These include gasoline and lighter hydrocarbons;

### Pigging activities and depressurisation – vapour recovery

- 4. Recover the vapours and liquids by piping to a vapour recovery and recompression system rather than routing to flare;
- 5. Ensure operating procedures are in place to prevent venting of vapours to atmosphere;

### Hydrocarbons from bitumen production

- 6. Incinerate vapours from bitumen blowing units and similar operations units rather than direct discharge to atmosphere;
- 7. Provide arrestment plant downstream of this incinerator where particulate emissions approach 50 mg/m<sup>3</sup>;

### VOCs from miscellaneous sources

- 8. Use vapour recovery to abate VOC releases where it is practicable to capture them and where possible they should be returned to fuel gas systems;
- 9. Use catalytic incinerators or flameless thermal oxidisers. They can typically achieve the

## **Fugitive emissions**

same or better destruction efficiency at a lower temperature. With incineration, the use of flame/detonation traps or other safeguards is essential.

#### **Refrigeration systems**

10. Avoid the use of refrigerants that are of significant environmental concern which will escape during operation. Best available techniques for gas dew-point control are to avoid the use of refrigerants;

#### **Carbon dioxide**

11. Use acid gas streams, containing carbon dioxide and a significant hydrocarbon content, in a suitable combustion process.

### 3.8 Fugitive emissions

### To Air

### Volatile organic compounds (VOCs) releases

The aim should be to prevent or minimise the release of VOCs. Because of the size, scope and nature of hydrocarbon processing on refineries, this presents a major challenge and requires an overall strategy and action at a process unit and plant item level. Most VOCs are released as fugitive losses from sources including valves, flanges, pump seals and equipment vents. A small simple refinery may have over 10,000 potential sources, larger complex refineries even more. The principal areas of fugitive loss are well known.

A fugitive release inventory should be established by:

 identifying all potential sources of VOC releases by establishing population counts of equipment components in line with up-to-date P & I drawings for processes. This survey should cover gas, vapour and light liquid duties;

- quantifying the VOC releases, initially as "baseline" estimates which are then refined;
- using appropriate dispersion modelling techniques to predict atmospheric mass flux and concentrations;
- employing environmental monitoring techniques, compare the predicted situation with the measured one.

Processes and facilities should be prioritised and loss assessments carried out on a rolling basis starting with the highest priority areas. Higher priorities are those involving gas or light liquids, especially at elevated temperature/pressure with valves that move frequently; also, tankage, loading and transfer (particularly of gasoline grade materials) points and effluent systems.

# **Fugitive emissions**

For process component fugitive releases, a permanent on-going Leak Detection and Repair (LDAR) programme should be implemented. It should provide estimates of fugitive VOC releases for monitoring returns and enable action to be taken to minimise releases.

### Leak detection and repair (LDAR)

Survey results show that leaks from glands on valves and pumps are responsible for 90% or more of estimated fugitive releases and that a small proportion of valves, virtually all on gas or high temperature light material streams, contribute almost the entire total.

### Indicative BAT

You should, where appropriate:

- 1. Use a Leak Detection and Repair (LDAR) programme for the control of fugitive releases;
- 2. Use low emission valve stem packing (500ppm) on critical valves, e.g. rising stem gate type control valves in continuous operation, particularly on gas/light liquid high pressure/temperature duties;
- 3. Use alternative proven types of low-release valves where gate valves are not essential, e.g. quarter turn and sleeved plug valves, both of which have two independent seals;
- 4. Use balanced bellows type relief valves to minimise valve leakage outside the design lift range and piping of reliefs to RFG or flare gas, normally via phase separation, without header back pressure;
- 5. Minimise the number of flanged connections on pipelines and use high specification jointing materials; use canned pumps or double seals on conventional pumps; piping of compressor seals, vent and purge lines to RFG or flare systems;
- 6. Use end caps or plugs on open ended lines and closed loop flush on liquid sampling points;
- 7. Minimise the releases to air from process hydrocarbon analysers, by optimising sampling volume/frequency and venting to RFG or flare systems;
- 8. Identify and, where possible quantify, significant fugitive emissions to air from all the specific relevant sources listed above, estimating the proportion of total emissions that are attributable to fugitive releases for each substance. Where there are opportunities for reductions, the Permit may require the updated inventory of fugitive emissions to be submitted.

### **3.9 Monitoring**

Continuous monitoring of emissions to air should be undertaken according to the following table:

# Monitoring

Process	Р	Parameters									
	Particulate matter	NOx	SO <sub>2</sub>	со							
Combustion processes burning fuel oil	Y	Y		Y							
FCCU Regenerators	Y	Y	Y	Y							
SRUs			Y								
Sour gas incinerators and furnaces			Y								
Bitumen Production unit			Y								
Gasification Unit	Y	Y	Y								

The Large Combustion Plant Directive requires continuous emissions monitoring equipment to be fitted to combustion plant to measure  $SO_2$ , NOx and particulates, depending on the thermal rating of the equipment.



### Annex 1 Emission benchmarks Annex 2 Other relevant guidance and abbreviations

Environment Agency

### 4. Annexes Annex 1- Emission benchmarks

### **Emissions to air**

The emissions quoted below are as daily averages based upon continuous monitoring during the period of operation. Care should always be taken to convert benchmark and proposed releases to the same reference conditions for comparison. Monitoring Guidance M2 explains how to convert measured values to reference conditions, see Annex 2.

Where emissions are expressed in terms of concentrations and where continuous monitors are employed, the limits are defined such that:

- not more than one calendar monthly average during any rolling twelvemonth period shall exceed the benchmark value by more than 10%;
- not more than one half hour period\* during any rolling 24 hour period shall exceed the benchmark value by more than 50%.

\* half hourly periods to commence on the hour and the half hour.

Where spot tests are employed:

• the half hour limit above shall be applied over the period of the test

• the mean of three consecutive tests taken during a calendar year shall not exceed the benchmark value by more than 10%. Note that processes, which come under the provisions of the Large Combustion Plant Directive or the Waste Incineration Directive, will also need to address the specific requirements of these directives.

The reference conditions of substances in releases to air from point-sources are:

For combustion gases:

- dry
- temperature 273K (0°C)
- pressure 101.3kPa (1 atmosphere)
- and adjusted to oxygen content of
- 3% v/v, dry for liquid and gaseous fuels burned at large boilers and furnaces,
- 15% v/v, dry for liquid and gaseous fuels burned at CI engines and gas
- turbines,
- 6% v/v, dry for solid fuels burned at large boilers and furnaces

For non-combustion gases:

- no correction for water vapour or oxygen content,
- temperature 273K (0°C)
- pressure 101.3kPa (1 atmosphere)

Achievable emissions to air are given in the following tables. Achievable releases shown under 'Fuel Systems and Combustion Plant' are the same as in the guidance note for Combustion Activities.

Refining Sub- Sector	Size	Unit Operation	Fuel	Ref %O <sub>2</sub>	Achiev 101.3 k			ations,	BAT decision			
					PM Total	SO <sub>2</sub>	NOx	N <sub>2</sub> O	СО	HCI	Other	
Oil production Onshore reception Facilities												
		Fluidised catalytic cracking		3	10	25	10- 20		20- 50			Wet scrubbing with low-NOx / de- NOx abatement technologies. Regenerative SO <sub>2</sub> wet-scrubbing Technology minimises raw material use and solid and liquid processing wastes.

Sulphur recovery			Required minimum 99.5% S recovery efficiency. Tail gas treatment. SRU availability should approach 100 %
Process heaters.			Refer to Sector Guidance Note for Combustion Activities
aglainara	ee 50 ote subject to confirma tion		Note: No correction for O <sub>2</sub>

Refining Sub- Sector	Size	Unit Operation	Fuel	Ref %O <sub>2</sub>		evable c kPa (at	oncentra ref O <sub>2</sub> )	ations,	BAT decision			
					PM Tota I	SO <sub>2</sub>	NOx	N <sub>2</sub> O	СО	HCI	Other	
Natural gas refining												Process heaters etc as 'Utilities'
Gasification												Refer to Sector Guidance Note for Combustion Activities
Utilities												
		Fuels systems & combustion processes										Refer to Sector Guidance Note for Combustion Activities

50- 100 MWt h	New	Liquid	3	15	175 (post 2008)	300	150	1-5	NH₃ 10	S BAT = Gasoil. SCLF requires 0.2% S, 0.1 % by 2008
	Retrofit 1%S	Liquid	3	50	1700 685	450	30- 50	1-5		S Opted out or small scale plant SCLF = 1% S(FRF). Opted in
	1%S +DSI									consider DSI IPC note states 685mgm <sup>-3</sup> . Eurelectric states
										200-850.

Refining Sub- Sector	Size	Unit Operation	Fuel	Ref %O₂			concent t ref O <sub>2</sub> )	rations, I )	BAT decision			
					PM Tot al	SO <sub>2</sub>	NOx	N <sub>2</sub> O	СО	HCI	Other	
	100- 300 MWth	New	Liqu id	3	15	200	150		150	1-5	NH₃ 5	S BAT = Gasoil. SCLF requires 0.2% S, 0.1 % by 2008 NOx BAT = BREF
Liquid		Retrofit 1% S 1%S + DSI	Liqu id	3	50	1700 400	450		30- 50	1-5		S Opted out or small scale plant SCLF = 1% S(FRF). Opted in consider DSI - IPC note states 685mgm-3. Eur states 400 so implies progress in technology, adopt Eur position NOx LCPD figure as per FRF >300 MWth New

>300 MWth	New	Liqu id	3	15	150	100	150	1-5	NH <sub>3</sub> 5	Large scale plant BAT = BREF
	Retrofit opt out opt in	Liqu id	3	50	1700 400	1400 450- 400 (300- 500M W)	30- 50	1-5		S Opted out BAT = SCLF(FRF). NOx FRF (JEP advice) Opted in LCPD sliding scale to 400mgm <sup>-3</sup> > 500MW
Other	Engines CI	Liqu id	15	50	112 66 from 2008	150	150			S 0.2% S, 150 NOx from IPC and correspondence with UK industry

Refining Sub- Sector	Size	Unit Operation	Fuel	Ref %O <sub>2</sub>	Achievable concentrations, mgm <sup>-3</sup> , dry at 0°C, 101.3 kPa (at ref O <sub>2</sub> ) BAT decision						BAT decision	
					PM Tot al	SO <sub>2</sub>	NOx	N <sub>2</sub> O	СО	HCI	Other	
	100- 300 MWth	New	Liquid	3	15	200	150		150	1-5	NH₃ 5	S BAT = Gasoil. SCLF requires 0.2% S, 0.1 % by 2008 NOx BAT = BREF
Liquid		Retrofit 1% S 1%S + DSI	Liquid	3	50	1700 400	450		30- 50	1-5		S Opted out or small scale plant SCLF = 1% S(FRF). Opted in consider DSI - IPC note states 685mgm <sup>-3</sup> . Eur states 400 so implies progress in technology, adopt Eur position NOx LCPD figure as per FRF >300 MWth New

>300 MWth	New	Liquid	3	15	150	100	150	1-5	NH <sub>3</sub> 5	Large scale plant BAT = BREF
	Retrofit opt out opt in	Liquid	3	50	1700 400	1400 450- 400 (300- 500M W)	30- 50	1-5		S Opted out BAT = SCLF(FRF). NOx FRF (JEP advice) Opted in LCPD sliding scale to 400mgm <sup>-3</sup> > 500MW
Other	Engines CI	Liquid	15	50	112 66 from 2008	150	150			S 0.2% S, 150 NOx from IPC and correspondence with UK industry

Refining Sub- Sector	Size	Unit Operation	Fuel	Ref %O <sub>2</sub>	Achievable concentrations, mgm <sup>-3</sup> , dry at 0°C, 101.3 kPa (at ref O <sub>2</sub> ) BAT decision							BAT decision
					PM Tota I	SO <sub>2</sub>	NOx	N <sub>2</sub> O	СО	HCI	Other	
		Gas turbines	Liquid	15		112 66 from 2008	125		100			IPC
		New gas turbines (incl CCGT)	Natural gas	15	5	10	50		100		NH <sub>3</sub> with SCR	BREF

Existing GTs(inc CCGT)DLN water or steam injection	Natural gas	15	5	10	75 110	1	100	NH₃ with SCR	BREF DLN H <sub>2</sub> O injection Eurelectric (120) and UK experience
Engines CI (Dual fuel)	Natural gas	15	20	50	100	2	450	NH₃ 10 with SCR NMV OCs 200	SCR IPC

Refining Sub- Sector	Size	Unit Operation	Fuel	Re f % O <sub>2</sub>	Achiev ref O <sub>2</sub> )	Achievable concentrations, mgm <sup>-3</sup> , dry at 0°C, 101.3 kPa (at ef O <sub>2</sub> )						BAT decision
					PM Total	SO <sub>2</sub>	NOx	N <sub>2</sub> O	СО	HCI	Other	
		Engines CI (Duel fuel)	Natural gas	15	20	50	150		150		NMV OCs 200	Lean burn IPC
		Engines SI	Natural gas	15			100		150			SCR IPC
		Engines SI	Natural gas	15			150		150			Lean burn IPC
		New boilers	Natural gas	3	5	10	100		100		NH₃ with SCR	

Existing boilers	Natural gas	3	5	10	100	100		IPC and BREF
All combustion plant	Industrial gas	3 or 15	BAT is gas cleanin g to remove fuel S and fuel PM	BAT is gas cleaning to remove fuel S and fuel PM	200	150		IPC (no BREF reference)

### **Emissions to water**

Releases, which are significant, include water treatment plant, boiler plant, ash handling and transport, and cooling towers. Where releases to water are necessary the flow weighted monthly average concentration in a final effluent will not exceed the achievable levels given below. The Environment Agency should set an annual mass emission limit for cadmium and mercury. Where automatic sampling systems are employed, limits may be defined such that:

not more than 5% of samples shall exceed the benchmark value.

Where spot samples are taken:

 no spot sample shall exceed the benchmark value by more than 50%

Substance	Range (mg/l)
Total hydrocarbon oil content (IR 8	1–3 see Note 2
method)	
Biochemical oxygen demand (BOD)	20–30
(5 day ATU @ 20°C)	
Chemical oxygen demand (COD)	50–100
(2 hour)	
Ammoniacal nitrogen (as N)	1–5
Phenol	0.1-0.5
Sulphide	0.5–1
Suspended solids (dried @ 105°C)	20–30
Metals	See TGN A4 and Note 3
PH	6–9
Temperature	Note 3
Chloride (Cl)	Note 3

#### Achievable releases to water (see note 1)

#### Notes:

- The levels given above are ranges achievable after effluent treatment using a biological treatment step and are not release limits. They are given on the basis of 95% of values not exceeding the relevant level.
- 2. Acid soluble oils should only be present at trace levels.
- 3. Statutory Instrument (1989) No 2286 gives limits for releases to water for cadmium and mercury.

Levels should be as low as practicable and reflect the quality of the receiving waters. Typical limits at the edge of a defined mixing zone in the receiving waters are to change the temperature of the receiving water by no more than 1°C and salinity by no more than 5%. The upper temperature limit for a discharge is around 40°C.

Substance	Range (mg/l)						
Hydrogen sulphide	0.1–1.0						
Ammonia (see Note 1)	1–10						

#### Achievable releases from sour water strippers

Notes: Where the water is fed to an ETP, higher levels of ammonia may be allowed as a source of nutrient to the biomass.

# Annex 2-Other relevant guidance and abbreviations

### **Annex 2- Other relevant guidance and abbreviations**

For a full list of available Technical Guidance and other relevant guidance see Appendix A of GTBR (see <u>http://publications.environment-agency.gov.uk/pdf/GEHO0908BOTD-e-e.pdf?lang=\_e</u>).

In addition to the guidance in GTBR the following guidance is relevant to this sector:

### 1. Guidance specific to this sector

- IPPC Reference Document on Best Available Techniques in the Gasification, Liquefaction and Refining Industry European Commission http://eippcb.jrc.es

- BREF on Waste Water and Waste Gas Treatment.

- US EPA Method 21(22) for process component losses and API methods (9) for tankage losses.

### 2. Relevant Directive

- The Sulphur in Liquid Fuels Directive, 1999/32/EC

### Abbreviations

API American Petroleum Insitute
ABGC Air Blown Gasification Cycle
AFNOR Association Francaise de Nomalisation
AMS Automated Measuring System
ASU Air Seperation Unit
AST Annual Surveillance Test
ASTM American Society for Testing and Materials
BOD Biochemical Oxygen Demand
BREF BAT Reference Document BSI British Standards Insitution CCA Climate Change Agreement CDU Crude Distillation Unit CEN Comitee Europeen de Normalisation CFB Circulating Fluidised Bed CHP Combined heat and power plant COD Chemical Oxygen Demand COMAH Control of Major Accident Hazards CPI Corrugated Plate Interceptor DIN Deutsches Insitute for Normung

# Annex 2-Other relevant guidance and abbreviations

**DPA** Direct Participant Agreement **ELV** Emission Limit Value **ESP** Electrostatic Precipitators **EQS** Environmental Quality Standard **ETP** Effluent treatment plant FCCU Fluidised Catalytic Cracking Unit GCC Gasification Combined Cycle **HCU** Hydrocracker Unit **HTW** High Temperature Winkler HSE Health Safety Executive **IGCC** Integrated Gasification Combined Cycle **ITEQ** International Toxicity Equivalents LDAR Leak detection and repair LNG Liquified Natural Gas LPG Liquified Petroleum Gas **MEG** Monoethylene glycol MHDS Methods for the Determination of Hazardous Substances **NIOSH** National Institute for Occupational Safety and Health

**OSHA** Occupational Safety and Health Administration **PPI** Parallel Plate Interceptor **RFG** Reformulated Gasoline **RFO** Refinery Fuel Oils **SCR** Selective Catalytic Reducer **SECp** Specific Energy consumption **SNCR** Selected Non-Catalytic Reducer **SNG** Subsitute Natural Gas **SRU** Sulphur Recovery Unit SWS Sour Water Stripping TAN Total Acid Number **TE** Technical Endorsements **TEG** Triethylene glycol **TSS** Total Suspended solids **TOC** Total Organic Carbon **UBA** Umweltbundesamt **US EPA** United States Enviromental Protection Agency **VDI** Verein Deustcher Ingenieure **VDU** Vacuum Distillation Unit **VOC** Volatile organic compounds

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