1.0 INTRODUCTION

This Guidance has been produced by the Environment Agency for England and Wales, with the Scottish Environment Protection Agency (SEPA) and the Environment and Heritage Service (EHS) in Northern Ireland - each referred to as “the Regulator” in this document. Its publication follows consultation with industry, Government departments and non-governmental organisations.

It aims to provide Operators and the Regulator’s officers with advice on indicative standards of operation and environmental performance relevant to the industrial sector concerned, to assist the former in the preparation of applications for PPC Permits and to assist the latter in the assessment of those Applications (and the setting of a subsequent compliance regime). The use of techniques quoted in the guidance and the setting of emission limit values at the benchmark values quoted in the guidance are not mandatory, except where there are statutory requirements from other legislation. However, the Regulator will carefully consider the relevance and relative importance of the information in the Guidance to the installation concerned when making technical judgments about the installation and when setting Conditions in the Permit, any departures from indicative standards being justified on a site-specific basis.

The Guidance also aims (through linkage with the Application Form or template) to provide a clear structure and methodology for Operators to follow to ensure they address all aspects of the PPC Regulations and other relevant Regulations, that are in force at the time of writing. Also, by expressing the Best Available Techniques (BAT) as clear indicative standards wherever possible, it aims to minimise the effort required by both Operator and Regulator to apply for and issue, respectively, a Permit for an installation.

1.1 Understanding IPPC

Integrated Pollution Prevention and Control (IPPC) is a regulatory system that employs an integrated approach to control the environmental impacts of certain listed industrial activities. It involves determination by the Regulator of the appropriate controls for those industries to protect the environment, through a single permitting process. To gain a Permit, Operators have to demonstrate in their Applications, in a systematic way, that the techniques they are using or are proposing to use, are the Best Available Techniques (BAT) for their installation, and meet certain other requirements, taking account of relevant local factors.

The essence of BAT is that the techniques selected to protect the environment should achieve an appropriate balance between environmental benefits and the costs incurred by Operators. However, whatever the costs involved, no installation may be permitted where its operation would cause significant pollution.

IPPC operates under **The Pollution Prevention and Control Regulations** (for equivalent legislation in Scotland and N Ireland see **Appendix 2**). The three regional versions of the PPC Regulations implement in the UK the EC Directive on IPPC (96/61/EC). Further information on the application of IPPC/PPC, together with

Government policy and advice on the interpretation of the English & Welsh Regulations, can be found in **IPPC: A Practical Guide** published by the Department for Environment, Food and Rural Affairs (Defra). Equivalent guidance on the Scottish Regulations is provided in **PPC Regulations: A Practical Guide (Part A Activities)**, published by the Scottish Executive and SEPA. The Department of the Environment, Northern Ireland has published equivalent guidance on its Regulations.

The BAT approach of IPPC differs from regulatory approaches based on fixed national emission limits (except where General Binding Rules or Standard Permits are issued). The legal instrument that ultimately defines BAT is the Permit, and Permits can only be issued at the installation level.

Indicative BAT standards are laid out in national guidance (such as this) and, where relevant, should be applied unless a different standard can be justified for a particular installation. BAT includes the technical components, process control, and management of the installation given in Section 2, and the benchmark levels for emissions identified in Section 3. Departures from those benchmark levels can be justified at the installation level by taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions.

Some industrial sectors for which national guidance is issued are narrow and tightly defined, whilst other sectors are wide and diffuse. This means that where the guidance covers a wide variety of processes, and individual techniques are not described in detail, the techniques (and their associated emission levels) which might constitute BAT for a particular operation, are more likely to differ, with justification, from the indicative BAT standards than would be the case for a narrow, tightly-defined sector.

If any mandatory EU emission limits or conditions are applicable, they must be met as a minimum, even where Bat for the installation would not by itself require such standards.

The BAT approach complements, but differs fundamentally from, regulatory approaches based on Environmental Quality Standards (EQS). Essentially, BAT requires measures to be taken to prevent emissions - and measures that simply reduce emissions are acceptable only where prevention is not practicable. Thus, if it is economically and technically viable to reduce emissions further, or prevent them altogether, then this should be done irrespective of whether or not EQSs are already being met. The BAT approach requires us not to consider the environment as a recipient of pollutants and waste, which can be filled up to a given level, but to do all that is practicable to minimise emissions from industrial activities and their impact. The BAT approach first considers what emission prevention can reasonably be achieved (covered by Sections 2 and 3 of this Guidance) and then checks to ensure that the local environmental conditions are secure (see **Section 4** of this Guidance and also Guidance Note **IPPC Environmental Assessments for BAT**). The BAT approach is therefore the more precautionary one because the release level achieved may be better than that simply required to meet an EQS.

Conversely, if the application of indicative BAT might lead to a situation in which an EQS is still threatened, a more effective technique is required to be BAT for that installation. The Regulations allow for expenditure beyond indicative BAT where necessary, and, ultimately, an installation will only be permitted to operate if it does not cause significant pollution.

Further advice on the relationship between BAT, EQSs and other related standards and obligations is given in **IPPC: A Practical Guide**, its Scottish equivalent, and also in Section 3.

The assessment of indicative BAT takes place at a number of levels. At the European level, the European Commission issues a “BAT reference document” (BREF) for each main IPPC sector. It also issues “horizontal” BREFs for a number of general techniques which are relevant across a series of industrial sectors. The BREFs are the result of an exchange of information between regulators, industry and other interested parties in Member States. Member States should take them into account when determining BAT, but they are allowed flexibility in their application. UK Sector Guidance Notes like this one take account of information contained in relevant BREFs and set out current indicative standards and expectations in the UK. At national level, techniques that are considered to be BAT should represent an appropriate balance of costs and benefits for a typical, well-performing installation in the sector concerned. They should also be affordable without making the sector as a whole uncompetitive, either within Europe or world-wide.

When assessing applicability of sectoral indicative BAT standards at the installation level, departures may be justified in either direction. Selection of the technique which is most appropriate may depend on local factors and, where the answer is not self-evident, an installation-specific assessment of the costs and benefits of the available options will be needed. The Regulator’s guidance **IPPC Environmental Assessments for BAT** and its associated software tool may help with the assessment. Individual installation or company profitability (as opposed to profitability of the relevant sector as a whole) is not a factor to be considered, however.

In the assessment of BAT at the installation level, the cost of improvements and the timing or phasing of that expenditure, are always factors to be taken into account. However, they should only be major or decisive factors in decisions about adopting indicative BAT where:

- the installation’s technical characteristics or local environmental conditions can be shown to be so different from those assumed in the sectoral assessment of BAT described in this guidance, that the indicative BAT standards may not be appropriate; or

- the BAT cost/benefit balance of an improvement only becomes favourable when the relevant item of plant is due for renewal/renovation (eg. change to a different design of furnace when the existing furnace is due for a rebuild). In effect, these are cases where BAT for the sector can be expressed in terms of local investment cycles; or

- a number of expensive improvements are needed. In these cases, a phasing programme may be appropriate - as long as it is not so drawn out that it appears to be rewarding a poorly performing installation.

In summary, departures by an individual installation from indicative BAT for its sector may be justified on the grounds of the technical characteristics of the installation concerned, its geographical location and the local environmental conditions - but not on the basis of individual company profitability, or if significant pollution would result. Further information on this can be found in IPPC: A Practical Guide and IPPC Part A(1) Installations: Guide for Applicants, or the equivalent Scottish Guidance.

The Regulators encourage the development and introduction of innovative techniques that advance indicative BAT standards criteria, ie. techniques which have been developed on a scale which reasonably allows implementation in the relevant sector, which are technically and economically viable and which further reduce emissions and their impact on the environment as a whole. One of the main aims of the PPC legislation is continuous improvement in the overall environmental performance of installations as a part of progressive sustainable development. This Sector Guidance Note describes the indicative BAT standards at the time of writing but Operators should keep up-to-date with improvements in technology - and this Guidance note cannot be cited as a reason for not introducing better available techniques. The technical characteristics of a particular installation may also provide opportunities not foreseen in the Guidance, and as BAT is determined at the installation level (except in the case of General Binding Rules (GBRs)), it is a requirement to consider these even where they go beyond the indicative Standards.

Indicative BAT standards apply, where relevant, to both new and existing installations, but it will be more difficult to justify departures in the case of new installations (or new activities in existing installations) - and for new activities, techniques which meet or exceed indicative BAT requirements should normally be in place before operations start.

For an existing installation, it may not be reasonable to expect compliance with indicative BAT standards immediately if the cost of doing so is disproportionate to the environmental benefit to be achieved. In such circumstances, operating techniques that are not at the relevant indicative BAT standard may be acceptable, provided that they represent what is considered BAT for that installation and otherwise comply with the requirements of the Regulations. The determination of BAT for the installation will involve assessment of the technical characteristics of the installation and local environmental considerations, but where there is a significant difference between relevant indicative BAT and BAT for an installation, the Permit may require further improvements on a reasonably short timescale.

Where there are departures from relevant indicative BAT standards, Operators of existing installations will be expected to have upgrading plans and timetables. Formal timescales for upgrading will be set as Improvement Conditions in the Permits. See **Section 1.4.2** for more details.

1.2 Making an application

For issue of a Permit a PPC Application has to:

- address the issues in Sections 2 and 3 of this guidance;
- assess the environmental impact described in Section 4 (and for England and Wales also in **Environmental Assessment and Appraisal of BAT (IPPC H1)**);
- demonstrate that the proposed techniques are BAT for the installation.

In practice, many PPC Applications have containted far more information than was needed for determination, yet have not addressed the areas that are most important - and this has led to extensive requests for further information. In an attempt to focus application responses to the areas of concern to the Regulator, Application forms (templates) have been produced by the Environment Agency, by SEPA and by EHS in N Ireland. In addition, as the dates for application have approached, the operators in most industrial sectors in England and Wales have been provided with Compact Discs (CDs) which contain all relevant Application Forms, technical and administrative guidance, BREFs and Assessment tools, hyper-linked together for ease of use.

For Applicants with existing IPC Authorisations or Waste Management Licences, the previous applications may provide much of the information for the PPC application. However, where the submitted Application refers to information supplied with a previous application the Operator will need to send fresh copies - though for many issues where there is a tendency for frequent changes of detail (for example, information about the management systems), it will be more appropriate simply to refer to the information in the Application and keep available for inspection on site, up-to-date versions of the documents.

For further advice see IPPC **Part A(1) Installations: Guide for Applicants (for England and Wales)** or PPC Part A Installations: Guide for Applicants (for Scotland) or the equivalent Northern Ireland guide for Applicants.

1.3 Installations covered

This Guidance relates to installations containing the activities listed below, as described in Part A(1) of Schedule 1 to the **The Pollution Prevention and Control Regulations**. The schedules of listed activities are slightly different in Scotland and Northern Ireland so for their equivalent Regulations see **Appendix 2**.

Installations covered within the scope of this guidance include: *(subject to notes)*

Part A(1)
Section 1.2 - Gasification, Liquefaction and Refining Activities,

(a) 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.

(c) NOT INCLUDED – Coking (Refer to S2 1.06 Carbonisation processes: coke manufacture)

(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.

(i) 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

The installation will also include **associated activities** which have a technical connection with the main activities and which may have an effect on emissions and pollution, as well as the main activities described above. These may involve activities 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.

Environment Agency advice on the composition of English or Welsh installations and which on-site activities are to be included within it (or them) is given in its guidance document **IPPC Regulatory Guidance Series No.5 - Interpretation of "Installation" in the PPC Regulations**. Operators are advised to discuss the composition of their installations with the Regulator before preparing their Applications.

1.4 Timescales

1.4.1 Permit review periods

Permits are likely to be reviewed as follows:

- for individual activities not previously subject to regulation under IPC or Waste Management Licensing, a review should be carried out within four years of the issue of the PPC Permit
- for individual activities previously subject to regulation under IPC or Waste Management Licensing, a review should be carried out within six years of the issue of the IPPC Permit

However, where discharges of Groundwater List I or List II substances have been permitted, or where there is disposal of any matter that might lead to an indirect discharge of any Groundwater List I or II substance, a review must be carried out within four years as a requirement of the Groundwater Regulations.

These periods will be kept under review and, if any of the above factors change significantly, they may be shortened or extended.

1.4.2 Upgrading timescales for existing plant

Unless subject to specific conditions elsewhere in the Permit, upgrading timescales will be set in the Improvement Programme of the Permit, having regard to the criteria for improvements in the following two categories:

1. *Standard "good-practice" requirements, such as, management systems, waste, water and energy audits, bunding, housekeeping measures to prevent fugitive or accidental emissions, good waste handling facilities, and adequate monitoring equipment*. Many of these require relatively modest capital expenditure and so, with studies aimed at improving environmental performance, they should be implemented as soon as possible and generally well within 3 years of issue of the Permit.

2. *Larger, more capital-intensive improvements, such as major changes to reaction systems or the installation of significant abatement equipment*. Ideally these improvements should also be completed within 3 years of Permit issue, particularly where there is considerable divergence from relevant indicative BAT standards, but where justified in objective terms, longer time-scales may be allowed by the Regulator.

Local environmental impacts may require action to be taken more quickly than the indicative timescales above, and requirements still outstanding from any upgrading programme in a previous permit should be completed to the original time-scale or sooner. On the other hand, where an activity already operates to a standard that is close to an indicative requirement a more extended time-scale may be acceptable. Unless there are statutory deadlines for compliance with national or international requirements, the requirement by the Regulator for capital expenditure on improvements and the rate at which those improvements have to be made, should be proportionate to the divergence of the installation from indicative standards and to the environmental benefits that will be gained.

The Operator should include in the Application a proposed programme in which all identified improvements (and rectification of clear deficiencies) are undertaken at the earliest practicable opportunities. The Regulator will assess BAT for the installation and the improvements that need to be made, compare them with the Operator's proposals, and then set appropriate Improvement Conditions in the Permit

1.5 Key issues

The Refinery Sector covers the range of oil and gas energy industries. Activity is centred upon the refinery operations, and the industry is dominated by the crude oil and related energy source prices. These have been subject to significant fluctuation and continue to have an uncertain future.

Refineries manage large quantities of raw materials and are also intensive consumers of utilities, such as energy and water. In storage processing of materials, refineries generate large quantities of emissions. 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.

Crude oils vary in composition and refineries are often limited to process a comparatively narrow range of crude oil slates. When switching from one crude oil to another within this range, emissions do not usually vary significantly. Consequently the type and quantity of refinery emissions to the environment from such operations can usually be predicted relatively accurately. However, from time to time, processing of different crudes can have unforeseen impacts on the performance of refinery processes; leading to an increase in emissions. The obligation for regulatory compliance remains with the Operator.

1.5.1 Emissions to the atmosphere

Power plants, boilers, heaters and catalytic cracking are the main sources of emissions of carbon monoxide and dioxide, nitrogen oxides (NO_X), particulates, and sulphur oxides (SO_X) to the atmosphere. 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. 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_2S, NH_3, BTX, Carbon disulphide (CS_2), carbonyl sulphide (COS), HF and metals as constituents of the particulates (V,Ni and others). Table 1 shows a very brief summary of the main pollutants emitted by a refinery, with their main sources.

TABLE 1: MAIN AIR POLLUTANTS EMITTED BY REFINERIES AND THEIR MAIN SOURCES

Main air	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_2O, NO. NO_2)	Process furnaces, boilers, gas turbines Fluidised catalytic cracking regenerators, CO boilers, Coke calciners, Incinerators, Flare systems
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 system, 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	See VOCs

Carbon dioxide (CO_2) is the greenhouse gas which receives most attention in the debate about global climate change. The main source of CO_2 emissions is the production of energy. Since the first oil crisis in 1973, refineries have made a concerted effort to enhance energy efficiency. Despite these energy conservation measures, refinery energy demand has increased due to tightened product specifications and a shift over the years from producing heavy fuel oils to transport fuels.

Carbon monoxide (CO) always appears as an intermediate product of the combustion processes and in particular occurs in below stoichiometric combustion conditions. However, the relevance of CO releases from refineries are not very high compared to CO_2.

Global warming will be a significant impact that should be addressed under climate change agreements and/or the EU Emissions Trading Scheme. In this context, PPC recognises the benefits of good combustion practice, such as CHP.

Oxides of nitrogen (NO_X), when emitted to the air, can combine with water and form a component of “acid rain”. Further, NO_X in combination with volatile organic compounds and sunlight, can lead to the formation of ground-level ozone. The source of NOx is mainly the combustion processes; during the combustion of fuel, nitrogen (mainly originating from the combustion air itself) is transformed to a mixture of NO_2 and NO. Combustion conditions play an important role here In controlling releases

Particulate emissions have become a focus of attention because of their potential adverse health effects. Particulate emissions are caused by combustion of fuel oils, especially when there is sub-optimal combustion. Another source is the catalytic cracker. Particulate emissions are often associated with metal releases.

Sulphur oxides (SOx), when emitted to the air, can combine with water and form a component of 'acid rain', having a long range impact. Within a short range of emission sources, sulphur dioxide impacts vegetation and the affects lining of the respiratory systems impacting health. The main source of SOx is the production of energy; during combustion, the sulphur in the fuel is transformed to a mixture of SO_2 and SO_3. Another source, typically smaller, is the flue gas from the sulphur recovery units. There is a direct relation between the sulphur in the feed to a combustion process and the sulphur oxides in its flue gas. Generally speaking the sulphur content of the refinery fuel pool is a delicate balance between energy required, the type of crude processed, the emission limits and economic optimisations. SOx emissions remain a key focus for refineries.

Volatile organic carbons (VOC), as mentioned above, can react with NOx in the presence of sunlight to form low-level atmospheric ozone. Furthermore, emissions of VOC can give rise to odour problems, which may result in complaints from nearby residents. The source of VOC emissions is the evaporation and leakage of hydrocarbon fractions during storage and distribution. Hydrocarbons may also be emitted during non-optimal combustion conditions, but these give only a small contribution.

Volatile organic carbons (VOC) include benzene and other aromatic hydrocarbons and polycyclic aromatic hydrocarbons. Benzene is a known human carcinogen; the main sources of it in the atmosphere are the petroleum and petrochemical industries and other combustion processes. Benzene reacts with other air pollutants and is broken down and either returned to the earth or becomes involves in the formation of photochemical smog. Whilst exposure to benzene at normal background concentrations is unlikely to have any adverse effect on human health, long term exposure to elevated levels, or short term exposure to elevated levels can harm health.

Many polycyclic aromatic hydrocarbons (PAHs) are known carcinogens and are ubiquitous in the environment, occurring naturally in some hydrocarbon mixtures deriving from minerals, such as coal or petroleum. They are also generated in processes involving the combustion of any organic matter, including fuels. Coal-tar pitch volatiles (CTPVs), which contain PAHs, are produced during coking, tar distillation, aluminium smelting and downstream uses of tar and pitch. These “CTPV” industries produce the highest exposures, in particular the coking process. Exposures on coke ovens are controlled by the use of respiratory protective equipment, due to the cost-prohibitive investment that would be needed to upgrade the few remaining ovens.

Individual sources of air emissions from particular processes are indicated in **Section 2.1 - In-process controls - in this Note, and further details are provided in the relevant BREF[1]**.

Section 2.2.4 of this Guidance Note covers relevant issues and, in addition, prevention and control of fugitive emissions is covered in the **Emissions from Storage BREF and in other relevant BREF**[1].

1.5.2 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. Refineries discharge waste water which originates from:

- Produced water, process water, steam and wash water. These waters have been in contact with the process fluids, and apart from oil, will also have taken up hydrogen sulphide (H_2S), ammonia (NH_3) and phenols. The more severe the conversion processes, the more H_2S and NH_3 are taken up by the process water. The process water is treated in several stages before discharge to the environment.
- Cooling water, once-through or circulating systems. This stream is theoretically free of oil. However, leakage into once-through systems, even at low concentrations, can result in significant mass losses because of the large volume of water involved.
- Rainwater from process areas. This type of water has not been in contact with the process fluids, but it comes from rainfall on surfaces which are possibly oil-polluted. It is often referred to as 'accidentally oil-contaminated' water and is typically treated prior to discharge to the environment.
- Rainwater from non-process areas. This stream is oil-free.

Oil and hydrocarbons are the main pollutants found in waste water generated by refineries. Other pollutants found in waste water generated by refineries are hydrogen sulphide, ammonia, phenols, benzene, cyanides and suspended solids containing metals and inorganic compounds (e.g. halides, sulphates, phosphates, sulphides). Table 2 gives a summary of the main water pollutants as well as their main sources.

TABLE 2: MAIN WATER POLLUTANTS (PARAMETERS) GENERATED BY REFINERIES
SOURCE: [ADAPTED FROM CONCAWE, 1999][20.43]

Water pollutant	Source
Oil	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain)
H2S(RSH)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking, lube oil, spent caustic
NH_3,(NH_4^+)	Distillation units, hydrotreatment, visbreaker, catalytic cracking, hydrocracking. lube oil. sanitary/domestic
Phenols	Distillation units, visbreakcr, 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), sanitarv/domestic
CN^- , (CNS^-)	Visbreaker, catalytic cracking, spent caustic, ballast water

TSS	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,

Refinery waste water treatment techniques are mature techniques, and emphasis has now shifted to prevention and reduction. Water re-use, reduction of water use and/or the concentration of pollutants in the water, can have effects in reducing the final emission of pollutants.

Effluent streams specific to individual process are identified in Section 2.1 and its sub-sections in this Note, and treatment techniques are covered in Section 2.2.2. More detail on available techniques is provided in the **Waste Water and Waste Gas Treatment BREF**[1].

1.5.3 Waste generation

The amount of waste generated by refineries is small if it is compared to the amount of raw materials and products that they process. Oil refinery waste normally covers three categories of materials:

- sludges, both oily (e.g. tanks bottoms) and non-oily (e.g. from waste water treatment facilities),
- other refinery wastes, including miscellaneous liquid, semi-liquid or solid wastes (e.g.contaminated soil, spent catalysts from conversion processes, oily wastes, incinerator ash,spent caustic, spent clay, spent chemicals, acid tar) and, non-refining wastes, e.g. domestic, demolition and construction.

Table 3 shows a summary of the main types of solid wastes generated in a refinery and their sources.

TABLE 3: MAIN SOLID WASTES GENERATED BY REFINERIES SOURCE: [USAEPA, 1995][20.44]

Type of waste	Category	Source
Oiled materials	oily sludges	tank bottoms, biotreatment sludges, interceptor sludges, waste water treatment
	solid materials	contaminated soils, oil spill debris, filter clay acid, tar rags, filter materials, packing, lagging, activated carbon
Non-oiled materials	spent catalyst (excluding precious	Fluid catalytic cracking unit catalyst, hydrodesulphurisation / hydrotreatment) catalyst, polymerisation unit catalyst, residue
	other materials	resins, boiler feed water sludges, desiccants and absorbents, neutral sludges from alkylation plants, FGD wastes
Drums and		metal, glass, plastic, paint
Radioactive waste (if used)		catalysts, laboratory waste, cold section scale
Scales		leaded/unleaded scales, rust

Type of waste	Category	Source
Construction/demoli		scrap metal, concrete, asphalt, soil, asbestos, mineral fibres, plastic/wood
Spent chemicals		laboratory, caustic, acid, additives, sodium carbonate, solvents. MEA/DEA (mono/di-ethanol amine), TML/TEL (tetra methyl/ethyl
Pyrophoric wastes		scale from tanks/process units
Mixed wastes		domestic refuse, green waste
Waste oils		lube oils, cut oils, transformer oils, recovered oils, engine oils

Oil retained in sludges or other type of wastes represents a loss of product and, where possible, efforts are made to recover such oil. Waste disposal depends very much on its composition and on the local refinery situation. Because of the high operating costs of waste disposal, much priority has been given to waste minimisation schemes.

Waste generation trends during the last ten years show that oily sludge production is declining, mainly through housekeeping measures, whereas biological sludge generation has increased as a result of increased biotreatment of refinery effluent. Spent catalysts production is also increasing through the installation of new hydrocrackers, hydrotreatment facilities and catalytic cracker dust collectors. For all these waste categories increased use is made of third party waste contractors for off-site treatment and disposal.

The Landfill Directive may also require specialist pre-treatment of residues before they can be landfilled.

Operators should assess their activities against the BAT criteria laid out in Section 2.4, Section 2.5, and Section 2.6 of this Guidance Note.

1.5.4 Soil and groundwater contamination

Most refineries have some areas that are contaminated by historical product losses. The PPC Site reporting exercise has the objective to identify areas of known or potential contamination. Current refinery practices are designed to prevent spillages and leaks to ground. In the past, the awareness of the potential risks of these contaminated areas was low. The two main topics here are prevention of new spills and remediation of historic contamination. As mentioned within the scope, soil remediation is not included in the scope of this document. Most oil fractions are biodegradable, given time. The approach to cleaning-up these contaminated areas has changed over the years. Increased knowledge about soil sciences and the difficulty of soil remediation on a site that is still in operation, has lead to the pragmatic approach of managing the risks of these contaminated sites to ensure their fitness for use and ensuring that pollution does not spread beyond the site.

The main sources of contamination of soil and groundwater by oil are typically those places along the handling and processing train of crude to products where hydrocarbons can be lost to the ground. These are commonly associated with the storage, transfer, and transport of the hydrocarbons themselves or of hydrocarbon-containing water. The possibility of contamination by other substances such as contaminated water, catalysts and wastes also exists.

1.5.5 Odour

Some of the substances produced or used in installations covered by this Note have the odour potential to cause offence to neighbouring communities. This is a key issue for some installations, though probably not for the majority in the sector. The issues are covered in the Odour section in this Technical Guidance Note (Section 2.2.6) and in more detail in **Horizontal Guidance Note H4 covering Odour**.[20.45]

1.5.6 Energy efficiency

Most refineries are very large users of energy and the direct or indirect release to air of combustion products often is the biggest single environmental impact arising from their production activities - but 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. All installations will need to demonstrate efficient energy use to meet PPC requirements. (See Section 2.7)

1.5.7 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. Guidance is provided in the Noise section in this Technical Guidance Note (Section 2.9) and in greater detail in the **Horizontal Guidance Note H3 covering Noise**[15].

1.5.8 Other environmental issues

Especially for refineries situated near residential areas, nuisance has become an issue of discussion with both local authorities and with representatives of the local population in so-called neighbourhood councils. Topics such as noise, light and smoke emission (flaring) and smell which directly impact the residents receive much more emphasis in these neighbourhood councils than the 'major' emissions (e.g. SO_2) which tended to receive more attention historically.

Nuisance by light can be caused through flaring at night by refineries and petrochemical plants located near densely populated areas.

Visual impact may be an important issue with local communities or to avoid intrusive impact. Cooling tower and stack plumes should minimise visual impact recognising the potential for colour and background effects e.g. SO_3 may lead to the appearance of a yellow plume.

Since the 1970s refineries have devoted considerable resources to increasing process safety, both in design and operation by training, procedures and personal protection equipment. 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.

Occupational health is included in the operational safety procedures aimed at protecting workers from exposure to toxic materials and providing them with all necessary facilities which contribute to their well-being and their sense of security and safety. Instructions, information exchange and training of personnel, the provision of personal protection equipment as well as strict adherence to stringent operational procedures have contributed to a steady decrease in accidents and health incidents. Typical refinery pollutants and products with a health risk include hydrogen sulphide, BTEX (of which benzene is the most prominent), ammonia, phenol, HF, NO_X, SO_x and particulates (including metal components), for which legally binding Maximum Acceptable Concentrations values prevail.

The design of the refinery installations and the process control systems needs 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 subsequent pre-programmed automated activation of pumps, relief systems, purging systems, flares and other equipment. Examples of such occurrences are utility failure, breakdown of equipment, a fire or an explosion. Emergency situations leading to direct spills occurring in parts of the plant which are neither fully contained nor fully automated (such as pipeline or tank bottom rupture) have to be addressed with standing emergency procedures. These are directed to minimisation and containment of the spills, followed by rapid clean-up in order to minimise the environmental impact. Reference may be made to the current site COMAH Safety Report.

1.6 Summary of releases

The Releases below are described down to the unit operation level. Table 1 in section 1.7 shows the hierarchy of sub-sectors, operations and unit operations within the Gasification, Liquefaction and Refining Sector.

1.6.1 Oil Production

From on-shore oil production, the following sources of waste water occur:

- produced water – highly saline water contaminated with free and emulsified hydrocarbons and suspended solids. Following treatment, this stream is normally reinjected into the crude oil reservoir and may be used to help maintain oil field pressures;
- wash water – water with hydrocarbon contamination. Normally disposed of with the produced water

Releases to the environment commonly associated with the processes described are listed in Table 4.

TABLE 4: POTENTIAL RELEASE ROUTES FOR PRESCRIBED SUBSTANCES AND OTHER SUBSTANCES WHICH MAY CAUSE HARM

Source Releases				Substances					
To:	Air	Water	Land	Hydro	Oxides ,	Oxides ,	Oxides ,	Organi	Spent catalyst

Prescribed substance defined in SI 472):	A	W	L
Other substances Which may cause harm:	a	w	l

Sweet Crude without stabilising					Aw	w	
Sweet crude with simple stabilising			A	A	Aw	w	
Sour crude with simple stabilising	A	A	A	A	Aw	w	
Sweet crude with complex facilities			A	A	Aw	w	l
Sour crude with complex facilities	A	A	A	A	Aw	w	l

1.6.2 **Oil Refining**

1.6.2.1 **Handling and storage of crude oil, liquid intermediates and products**

Potential releases into air 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.

Pollutants found in waste water from refineries include hydrocarbons dissolved and free (insoluble), suspended solids, phenols, sulphides, chlorides, cyanides, ammonia and certain heavy metals.

Potential releases into land include hydrocarbon contaminated sludges from storage tanks.

1.6.2.2 **Crude oil atmospheric and vacuum distillation**

Potential releases into air are from:

- pressure relief valves on column overheads;
- poor containment in overhead systems including barometric sumps and vents;
- glands and seals on pumps, compressors and valves;
- flue gases from process heaters;
- de-coking vents from process heaters;
- venting during clean out procedures;
- sour water and waste discharges.

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

Potential releases into land are sludges from cleaning out desalters and other vessels.

1.6.2.3 Hydrogen Consuming Processes

Potential releases into air include 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 procedures or during cleaning operations;
- sour water and waste discharges.

Potential releases into water include hydrocarbons and sulphur compounds from spillages and leaks, particularly from sour water lines. Aqueous effluents arising from these types of process operation contain high concentrations of hydrogen sulphide and ammonia. The effluent is therefore fed to the SWS prior to being routed to the effluent treatment plant. During hydrocracking a low-volume, dirty effluent is produced containing ammonia and hydrogen sulphide, which is directed to the SWS.

The potential releases into land are from disposal of spent catalysts.

1.6.2.4 Gasoline Production Processes

Catalytic reforming

Potential releases into air include hydrocarbons from pressure relief valves and leakages. Hydrocarbons and dust releases may arise from venting during catalyst regeneration and replacement procedures and during clean out operations. Hydrogen chloride may also be released during catalyst regeneration. 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.

The potential releases into water include hydrocarbons from spillages and leaks.

There are no significant potential releases into land.

Fluidised catalytic cracking

Potential releases into air are as follows:

- 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 lead to releases of carbon moNOxide, smoke and, if heavy fuel oil is used in the feed furnace, particulate matter;
- 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 may be releasid from pressure reliefs, storage and handling operations, spillages and water discharges.

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

Potential releases into land are of catalyst in the form of fines from particulate matter arrestment equipment and intermittent spent catalyst discharge

Hydrogen fluoride alkylation

Potential releases into air are as follows:

- 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, if heavy fuel oil is used, particulate matter;
- hydrocarbons may be released from pressure reliefs, storage and handling operations, spillages and water and waste discharges;
- halogens or compounds may be released from pressure reliefs, vent gas and spillages;
- acid soluble oil may be released from process shut-down ponds during maintenance work, particularly the de-scaling of pipes conveying hydrogen fluoride. This may be odorous.

Potential releases into water are of hydrocarbons from separator drains (surge drum, accumulator, dryer) and spillages, and of acidic effluent containing dissolved and suspended chlorides and fluorides from the settlement pit or the process shutdown ponds.

Potential releases into land are of hydrocarbons from spent molecular sieves, carbon packings and acid soluble oil, and inorganic fluorides and chlorides from treatment stages

Isomerisation Introduction

Potential releases into air are of 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.

Potential releases into water are of hydrocarbons from reflux drum boot drain and spillages and of spent sodium hydroxide from the scrubber system.

Potential releases into land are of hydrocarbons from spillages/contaminated molecular sieves and catalyst

Catalytic polymerisation

Potential releases into air are of 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.

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

Potential releases into land are of acids in solid form and hydrocarbons from spent catalyst

Aromatics production

Potential 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.

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

Etherification

Potential 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.

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

Potential releases into land are of spent resins contaminated with hydrocarbons

1.6.2.5 LPG Recovery and Sweetening

Liquefied petroleum gas (LPG) production

Potential 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.

Potential releases into water are of hydrocarbons from spillages.

Potential releases into land are of hydrocarbons from contaminated spent molecular sieves

Chemical treatment (sweetening) processes

Potential 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.

1.6.2.6 Bottom Barrel Processes and Lubes

Visbreaking (mild thermal cracking)

Potential releases into air are of oxides of sulphur, oxides of nitrogen and carbon dioxide from the combustion of sulphur-containing fuels in the cracking furnace. Incomplete combustion may lead to releases of carbon monoxide and smoke, and particulate matter 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.

The potential releases into water are of hydrocarbons and sulphur compounds from the sour water drain, from reflux drums and spillages.

Potential releases into land are of hydrocarbons and sulphur compounds in spent amine solution sludges

Petroleum coke production

Potential releases into air are as follows:

- oxides of sulphur and nitrogen and carbon dioxide from the combustion of sulphurous fuels/feeds in the coking furnace, calciners and incinerator;
- incomplete combustion may lead to releases of carbon moNOxide, smoke and, if heavy fuel oil is used, particulate matter. Incomplete combustion in the incinerator may lead to the release of 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;
- particulate matter may be released from kiln gas cleaning system, rotary cooler gas cleaning system, coke handling and storage and loading operations.

Potential 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.

The potential releases into land are of hot oil blowdown sludges containing hydrocarbons

Bitumen production

Potential releases into air are as follows:

- oxides of sulphur and nitrogen and carbon dioxide from the combustion of sulphurous fuels/feeds in the coking furnace, calciners and incinerator;
- incomplete combustion may lead to releases of carbon moNOxide, smoke and, if heavy fuel oil is used, particulate matter. Incomplete combustion in the incinerator may lead to the release of 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;
- particulate matter may be released from kiln gas cleaning system, rotary cooler gas cleaning system, coke handling and storage and loading operations.

Potential 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.

The potential releases into land are of hot oil blowdown sludges containing hydrocarbons

Lubricating oil production

Potential 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.

Potential 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.

Potential releases into land are from disposal of spent hydrofining catalyst

1.6.2.7 Ancillary Processes

Odorising of natural gas or LPG

Potential 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 if these techniques are used, including a small release of sulphur dioxide from combustion of the odorant.

Potential releases into land include solid waste such as materials used to absorb odorant spillage.

Sour water stripping

Potential 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.

The potential 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

Potential 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. The stack gases discharged from the incinerator may contain sulphur compounds, mainly sulphur dioxide, from unrecovered sulphur, oxides of nitrogen from gas burning and ammonia destruction, smoke and particulate matter. 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 to air through the flare system.

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

Potential releases into land are from the disposal of spent catalyst (normally bauxite) and solid sulphur waste and spillages.

1.6.3 Natural Gas Refining

From refining of natural gas the main process source of waste water is:

- condensed steam from glycol or methanol regeneration plants, contaminated with glycol or methanol, hydrocarbons, amines and mercaptans. Generally it 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.
- In addition to these continuous process flows, contaminated effluent arises from site drainage (storm and fire water), ballast water from shipping, cooling water, boiler blowdowns and water treatment / demineralisation regeneration water.

Releases to the environment commonly associated with the processes described acre listed inTable 5.

TABLE 5 POTENTIAL RELEASE ROUTES FOR PRESCRIBED SUBSTANCES AND OTHER SUBSTANCES WHICH MAY CAUSE HARM

SOURCE RELEASES	Substances									
To: Air Water Land Prescribed substance defined in S1472): A W L Other substances Which may cause harm: a w l	Hydorgen Sulphids	Oxides of sulphur	Oxides of Nitrogen	Oxides of carbon	Organic compounds	Oily waters	Nitrogen	Spent catalysts/adsorbents	Sand/corrosion products	Acids/alkalis/salts etc
On-shore reception	A*				A*w*	*w*			*l*	
Gas treatment processes	A*		A	A	A*w*	*w*		*l*		*l*
Acid Gas processes	A*	A*	A	A	A*w*	*w*		*l*		
Nitrogen removal	A*				A		a			
Hydrocarbon removal					A*w*	*w*				
Gas compression			A	A	A					
Condensate treatment			A	A	A*w*			*l*		*w*
Field water treatment					*w*	*w*				
Flares/vents	A*	A*	A	A	A					
Gas storage sites	A	A	A	A	A*w*	*w*		*l*		

*if sour gas is being processed

1.6.4 Gasification

Releases to the environment commonly associated with the processes described are listed in Table 6

TABLE 6 POTENTIAL RELEASE ROUTES FOR PRESCRIBED SUBSTANCES AND OTHER SUBSTANCES WHICH MAY CAUSE HARM

SOURCE RELEASES	Substances									
To: Air Water Land Prescribed substance defined in S1472): A W L Other substances Which may cause harm: a w l	Particulate Matter	Oxides of Sulphur	Oxides of Nitrogen	Oxides of Carbon	Organic Compounds	Acids / Alkalis / Salts Etc	VOC's	Hydrogen Sulphide	Ammonia	Metals and their salts

Raw Materials, Storage and Handling	A				awl		A			
Water Treatment	w				W	w				Ww
Slag / Ash Handling	A									
Gas handling and treatment	A	A	A	A	A		A	A	A	
Salt Recovery	A				lw					
Waste water treatment	w			A	Ww	w			w	
Site drainage (including rainwater)	w				w					
Gas turbine exhaust (GCC)	A	A	A	A			A			
Boiler blowdown	w					w				w

1.6.5 Utilities

1.6.5.1 Fuel systems and combustion processes

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

Releases to land may result from routine collection of grit and dust and arisings during cleaning procedures

1.6.5.2 Flares

Potential releases into air are products of combustion or incomplete combustion, for example soot or carbon particles, and emissions from sour water from flare knock out pots and water seals when sour gas is flared in an emergency. Because of the very low odour threshold of hydrogen sulphide and other gaseous sulphur compounds, sour gas flaring is a potential cause of odour release.

Potential releases into water are of hydrocarbons, sulphur and nitrogen compounds from water drain, knock-out vessels and water seals

1.6.5.3 Aqueous effluent treatment

Potential releases into air are of hydrocarbons by evaporation from exposed surfaces.

Potential 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.

Potential releases into land are 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

TABLE 7 GASIFICATION, LIQUEFACTION AND REFINING SECTION HIERARCHY

Level 1 IPPC Guidance Sector	Level 2 Sub-Sectors	Level 3 Operations	Level 4 Unit Operations	Licensor or like Terminology
Gasification, Liquefaction and Refining Sector	Oil Production	On-shore Reception Facilities	Sweet crude oil without stabilising facilities	
			Sweet crude oil with simple stabilising facilities	
			Sour crude oil with simple stabilising facilities	
			Sweet or sour crude oil with complex stabilising and sweetening facilities	
	Refinery [Refer to Refinery Schematic]	Handling and storage of crude oil, liquid intermediates and products	Crude Oil/Atmos. Residue Import & Storage	
			Intermediates/Products Storage & Export	
		Crude oil atmospheric and vacuum distillation	Desalting	
			Crude Distillation Unit	
			Vacuum Distillation Unit	
			Gas Plant	
		Hydrogen consuming processes	Hydrotreating Naphtha Hydrotreating	UOP Unionfining
			Kerosene Hydrotreating	
			Diesel Hydrotreating	
			Residue Hydrotreating	Chevron Lummus Global RDS/VRDS, UOP (RCD Unionfining. Catalytic Dewaxing)
			Hydrocracking	Iso-cracking, UOP Unicracking, Chevron Lummus LC Fining
		Gasoline Production Processes	Catalytic Reforming	UOP Platforming
			Fluidised Catalytic Cracking	KBR FCCP, UOP FCCP, Deep Cat. Cracking, RFCC Process*
			Hydrogen Fluoride Alkylation	UOP HF, ConocoPhillips ReVAP
			Isomerisation Introduction	UOP (Bensat, Butamer, Penex, TIP & OTZI, Par-Isom)
			Catalytic Polymerisation	NExOCTANE
			Aromatics production	UOP (Sulfolene, THDA, Isomar, Parex, Tatoray), BP-UOP (Cyclar)
			Etherification	UOP Oleflex, Hüls, UOP (Ethermax, olefin isomerisation, Oxypro)
		LPG Recovery and Sweetening	Liquefied Petroleum Gas (LPG) production	
			Chemical treatment (sweetening) processes	Belco EDV wet scrubbing, Conocophillips S Zorb
			FCC Naphtha Merox	UOP Merox
			Kerosene Merox	UOP Merox
		Bottom Barrel Processes and Lubes	Visbreaking (mild thermal cracking)	FW/UOP Visbreaking
			Petroleum Coke production	Conocophillips delayed coking, FW delayed coking,
			Bitumen production	
			Lubricating Oil production	
			Gasification	

		Ancilliary Processes	Hydrogen Plant	FW H2 Production
			Odorising of natural gas or LPG	
			Sour water stripping	
			Sulphur recovery	
	Natural Gas Refining	Off-shore Gas Handling and On-shore Reception		
		On-shore Gas Treatment		
	Gasification			
	Utilities	Fuel Systems and Combustion processes		
		Flares		
		Aqueous Effluent Treatment		

* RFCC Process Licensors are Stone & Webster-Institut Francais du Petrole Fluide

1.7 Technical overview

Table 7 shows the sub-sectors, operations and installations included within the Gasification, Liquefaction and Refining Sectors. The following sections briefly describe processes involved at the Unit Operation level of this hierarchy.

1.7.1 Oil Production

1.7.1.1 Introduction

A number of on-shore oil fields are producing crude oil by pumped extraction from underground oil-bearing reservoirs (geological structures containing hydrocarbons). Some fields produce oil via an individual isolated well site, but the majority have a number of well sites producing oil from a specific reservoir or a number of adjacent reservoirs. Well fluids, which are mixtures of gas, saline water and oil, are brought up to ground level using downhole pumps delivering via well head control equipment. The fluids are either delivered into well site storage tanks for onward transfer by road tanker or pumped through a pipeline to a local gathering centre for collection and initial processing.

The objectives of initial processing are to separate the fluids, to stabilise, sweeten and dry the oil as necessary for sale to the oil refining industry, to make appropriate use of any gas or LPG by -product streams and to dispose of produced water. Each oil field has a different fluid composition. The gas/water/liquid hydrocarbon ratio and the content of acid gas impurities (eg hydrogen sulphide) all vary, depending upon the field. An important distinction is made between "sweet" and "sour" oil, the former being oil which is substantially free from offensive odour and from which the associated gas typically contains less than 20mg/m^3 of H2S.

The following process descriptions cover the typical on-shore operations for both sweet and sour oils at different levels of complexity, ranging from small individual well sites with storage to complex and substantial gathering facilities.

On certain fields, wells may cease operating (typically due to excessive water cut) to allow the oil quantities to increase and make the well economically viable to work again. Such wells can remain unoperated for a number of years but under PPC could still remain active hence no site closure is considered. When bringing wells back into use testing is required to confirm it is viable to reopen. Appropriate containment for associated test tanks and systems is required.

Inspectors should be aware that naturally occurring radionuclides are present in the fluids produced from some fields or wells. These typically occur as radioisotopes of lead, bismuth or polonium found as solids in the produced water and although present at low concentrations, they may "plate" out on some processing equipment and may be concentrated in deposited scale or sludge. Depending upon their activity level, the accumulation and disposal of the resulting solids may need to be subject to separate authorisation under the Radioactive Substances Act 1993.

1.7.1.2 Sweet crude oil without stabilising facilities

See Figure 1. Well fluids are pumped at low production rates, normally by mechanical beam and rod pump ("nodding donkey"), direct to storage tanks from the wells. The amounts of associated gas and water are usually relatively small. In the tanks, most of the gas comes out of solution and is released to air through a vent pipe. Such facilities are usually too small or remote for pipeline transfer to a treatment centre and the wet depressurised oil is stable enough for it to be collected at intervals by road tanker for delivery to a gathering centre for processing. The facilities are usually unmanned but are subjected to regular inspection by production personnel.

1.7.1.3 Sweet crude oil with simple stabilising facilities

See Figure 2. Well fluids are received on-site direct by pipeline from larger outlying wells and wells on-site or by road tanker delivery from small remote sites. The fluids are combined, compressed and heated to a controlled temperature to effect phase separation using a direct or indirect heater, typically fired with process gas or gas oil. Combustion products are vented. De-emulsifiers are added to aid separation, which is usually in two or three stages, at decreasing pressure. The separated saline water is degassed, any oil or sand is removed, and is routed to a holding tank for re-injection into the reservoir (after biocide addition) or disposal by road tanker. The gas may be used for fuelling heaters, generating electricity, direct sale, or re-injection to reservoir, with any surplus being flared. The stabilised oil may be routed to stripping/degassing or desalting if required and then passes to storage and thence to loading facilities, or may be pumped direct to export, where this is by pipeline.

1.7.1.4 Sour crude oil with simple stabilising facilities

See Figure 2. Sour crude oils have to be stabilised to avoid subsequent release of sour gas; the process is similar to Section 1.7.1.3 above except that separated gas is sour and requires special treatment. If gas quantities are small and gas sweetening is not appropriate, it is not normally used as fuel gas or sold, instead a suitable substitute such as LPG or gas oil is used as fuel while the separated gas is destroyed by suitably efficient combustion, typically incineration, along with other sour gas, eg that vented from pressure reliefs and tank storage or displaced from filling of oil product tankers.

1.7.1.5 Sweet or sour crude oil with complex stabilising and sweetening facilities

See Figure 3. Where larger quantities of oil are being produced and/or collected at a gathering centre, economic factors may favour the installation of complex integrated stabilising and sweetening facilities, including a gas export system. This is particularly likely where high gas production quantities are involved as the operator will have a maximum gas flaring consented quantity as a condition of the site production licence. The size and scope of the process will depend on circumstances but will include phase separation, as described in Section 1.7.1.3, with the separated gas being compressed and passed to sweetening, and if appropriate, fractionation, to separate the lighter hydrocarbons into saleable fractions as appropriate, eg natural gas (methane) and LPG (propane and butane). Gas sweetening is carried out by an acid gas sulphur removal process such as absorption, adsorption or reaction. The processes which may be used for this are described in sections 1.7.3.2 and 0 below. Typically, amine scrubbing is used where high acid gas concentration is involved, while molecular sieve adsorption or zinc oxide reaction are favoured for treatment of low concentrations. Quantities of sulphur recovered do not normally justify an associated on-site sulphur recovery unit and the rich acid gas stream produced by the regeneration of rich amine solution or molecular sieve adsorbent may be incinerated as in Section 1.7.1.4 above. Spent zinc oxide is returned occasionally to primary zinc manufacture, where sulphur can be recovered, and replaced by fresh bed material.

Where gas quantities are too small to merit off-site sales and hence sulphur removal, but sufficient for use as fuel gas, modern power generating gas turbines are efficient at combusting low H2S concentrations in unsweetened gas and may therefore be used in place of incineration.

An emerging alternative technique for extracting low acid gas concentrations, developed initially off-shore, is the "fixing" of hydrogen sulphide by reaction with a water soluble and degradable alkanolamine derivative which is acceptable for adding to produced water and disposal by re-injection. This may be carried out by mixing the metered fixing agent into incoming crude oil prior to separation, so that the fixed sulphur dissolves into the water phase and separates out with it.

Where the sweetened gas is solely to be used on-site it is then routed to a fuel main to supply process/utility heaters, incinerator support fuel, flare pilots and any blanketing uses.

Gas that contains significant quantities of higher hydrocarbons above methane and which is required to be brought up to British Gas specification for export to the transmission system is dried and then passed to a fractionation process. This uses successive refrigerated distillation columns and is similar to the description of LPG production given in section 1.6.2.5 below. Product gas arises as the overheads from the first column, with butane and propane overhead streams from subsequent columns routed to storage/export, and the final column bottoms product (C5 and higher) being blended into the stabilised crude oil product. The product gas stream is compressed, chilled and passed through a knock-out pot to remove residual liquids. If required, it is odorised as described in section 1.6.2.7 below, before being metered into sales gas export. Fuel gas for on-site uses as above is supplied from appropriate sources, including the revaporised knock-out liquids, sales gas and separator off-gas where this is not sour. Sweet gas may also be used to strip stabilised crude oil of any residual dissolved hydrogen sulphide prior to export of the oil.

Separated produced water is treated as described in Section 1.7.1.3 above and is normally reinjected into dedicated wells along with any additional water which may be required to maintain pressure in the oil producing zones.

On a complex facility as described above, significant support facilities are also normally present. These may include emergency gas relief and flare systems, electricity generation using gas turbines, refrigeration and other utilities.

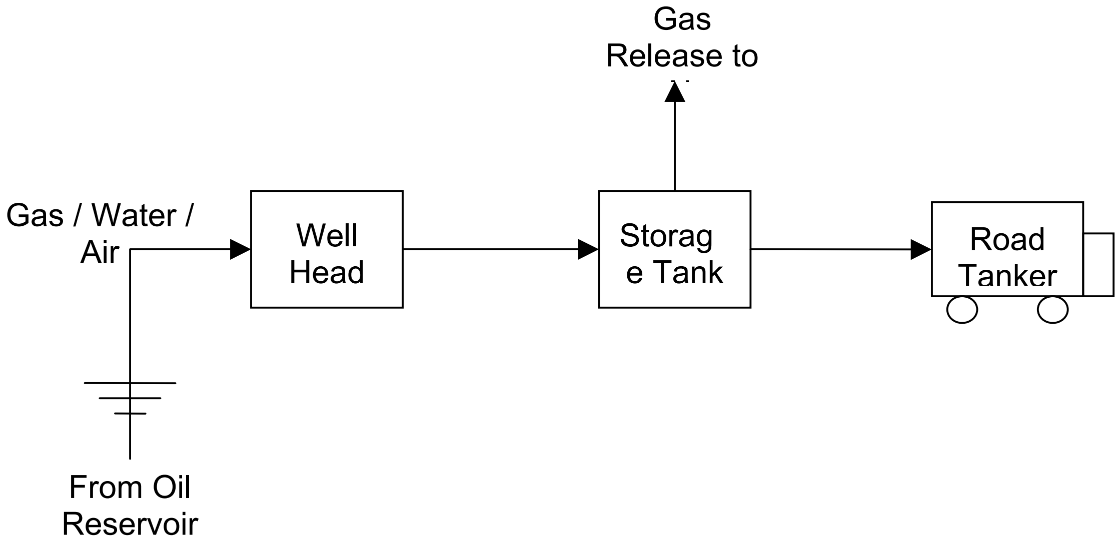

FIGURE 1: SWEET CRUDE WITHOUT STABILISATION

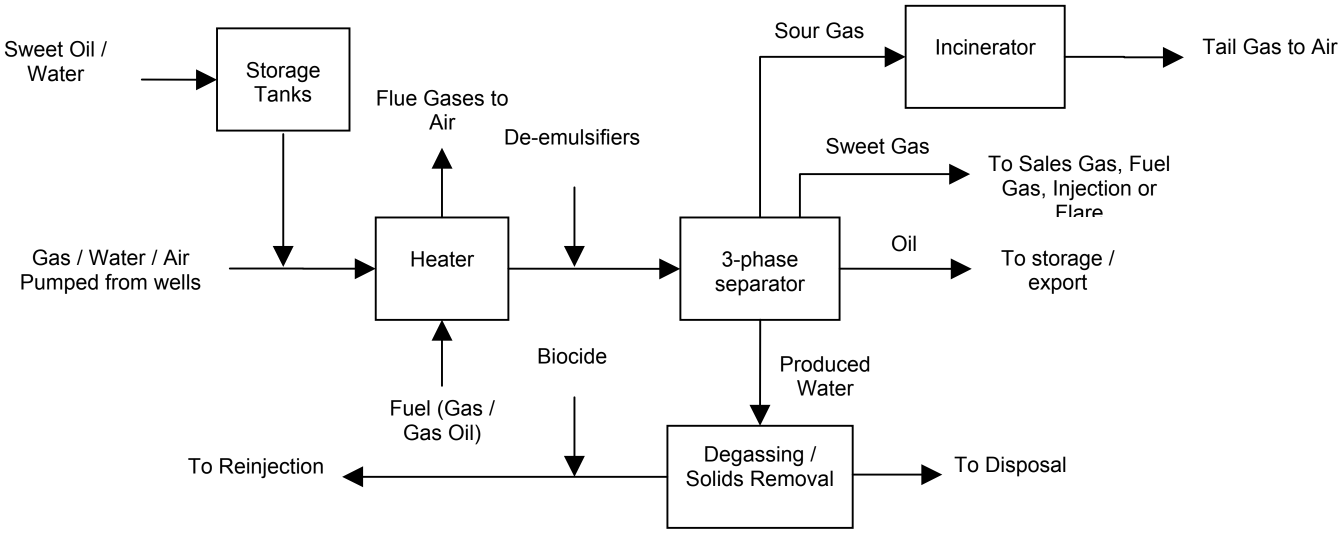

FIGURE 2: SWEET/SOUR CRUDE WITH SIMPLE STABILISATION

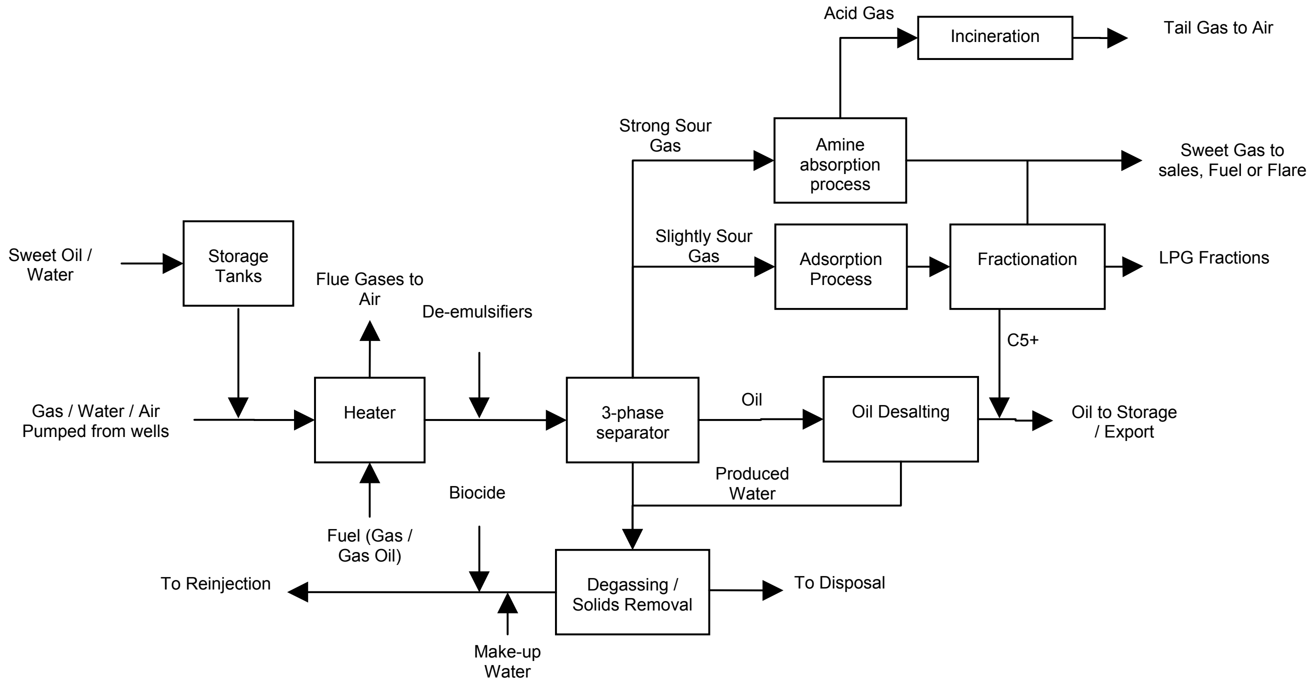

FIGURE 3: SWEET/SOUR CRUDE WITH COMPLEX FACILITIES

1.7.2 Refining Processes

The refining of crude oil or its derivatives into petroleum products is a complex activity which cannot be achieved in a single industrial process. It is first necessary to separate the feedstock, which is typically a blend of crude oils from more than one source, into fractions of different boiling point. Each fraction is then treated differently to upgrade its quality into saleable products using a series of individual processes. A simplified presentation of the major processes is shown in Figure 4 below, which also indicates some of the main relationships between them. These processes, their potential release routes to the environment and the techniques for controlling releases considered to represent best available techniques (BAT) at the time of publication are briefly described in this Note using simplified block diagrams to aid the text.

Refineries operating in England and Wales comprise different combinations of these processes in scale and complexity which vary considerably from only a small number of processes producing a limited range of products to the complete complex refinery with a large output of virtually all products. The simple operations are typically characterised by the use of mainly physical separation processes such as distillation with only limited use of conversion processes such as mild hydrotreating and reforming. Complex refineries make extensive use of conversion processes such as severe hydrotreating and catalytic cracking in order to shift their product spectrum towards the higher value and lighter products. Potential releases from the complex refineries are generally greater in scale and scope.

Refineries are subject to many business pressures, including the environmental impacts of the uses of their products as well as their processes, and the industry's response to these pressures will influence their future configuration. Of particular note will be the effects of the probable long-term shift to higher sulphur content feedstocks at a time when their product range is changing away from the heavy end products which have typically been a "sink" for sulphur. Remaining products will be constrained to carry much less sulphur to the users, while releases from the refinery must also be reduced. Some processes will be favoured by this transition, notably hydrotreating and other conversion processes, sweetening and sulphur recovery.

The changing market demand on refineries to provide, for example, a greater proportion of light products and regulatory requirements such as the Auto Oil Programme for products containing lower levels of sulphur results in a greater need for hydrogenation processes and removal of sulphur compounds. The additional hydrogen requirement will change the hydrogen balance in the refinery and may require installation of reforming or gasification units. Additional capacity for sulphur recovery may be needed. Some of these changes will tend to increase refinery fuel consumption.

Table 7 above shows the hierarchy of sub-sectors, operations, and installations within the Gasification, Liquefaction and Refining Sector. In this section each of the major refinery unit operations (level 4) are briefly described below.

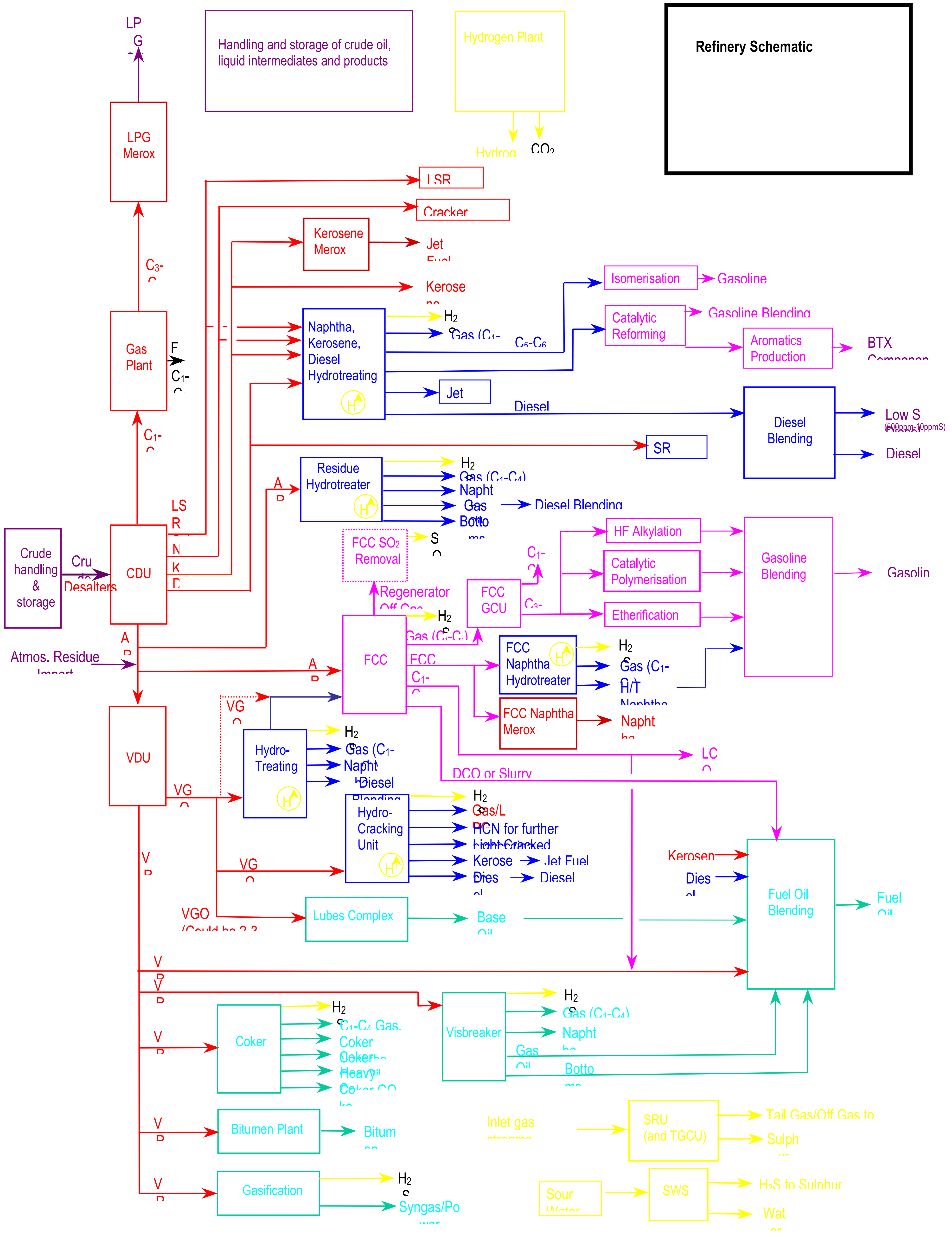

FIGURE 4: OVERALL REFINERY BLOCK FLOW DIAGRAM

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

Crude oil is normally shipped into refineries through marine terminals but can also arrive via pipeline or rail/road vehicles. Unless properly handled in enclosed systems crude oil can easily give rise to hydrocarbon releases to air. These can be highly odorous when sour crudes (ie of high sulphur content) are involved. Similarly, to avoid such releases, intermediates and final products should be handled and stored in appropriate equipment.

Releases to air from seagoing ships are not within the control of the Environment Agency. They can involve significant amounts of hydrocarbons and may cause considerable nuisance if the ship is not equipped with vapour locks for dipping/sampling operations, or if correct procedures are not used to avoid gas venting from sour crude cargoes, while it is lying alongside the jetty. (The largest releases occur when ships are being re-loaded and vapours are displaced. It is anticipated that international provisions will be proposed for control and recovery of such releases in 1996.)

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.21 Storage and handling of refinery materials

1.7.2.2 Crude oil atmospheric and vacuum distillation

The initial process in refineries is one of the most important and consists of distilling the crude oil into fractions, or cuts, of various boiling ranges which then go forward as products to finishing processes, intermediates for conversion processes, or residual materials as fuels. Light and heavy cuts receive atmospheric pressure distillation alone while bottoms, ie residue, are vacuum distilled as a prelude to conversion/cracking.

Desalting

The crude oil normally passes first to a desalter where fresh and/or re-cycled water is mixed with crude oil to extract soluble salts and then coalesced and separated.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.9 Desalting

Atmospheric Distillation

The desalted crude oil passes through heat exchangers and a process heater to a distillation tower operating at just above atmospheric pressure.

Various side streams are taken from the tower, sometimes into secondary fractionating or stripping columns, corresponding with normal product ranges such as light and heavy naphtha, kerosene, gas oils and bottoms (atmospheric residue). Refineries obtain some flexibility in operation by changing side stream cut points and hence their ratio of light to middle distillates, within the limits set by product specifications.

The overhead stream from the atmospheric distillation tower contains hydrocarbons normally gaseous at atmospheric pressure, light hydrocarbons, steam injected to the column and possibly traces of hydrogen chloride and hydrogen sulphide and organic sulphur compounds. For corrosion control, ammonia and other corrosion inhibitors may be injected into this stream. This stream is condensed and the incondensibles are passed to further separation or the refinery fuel gas system. The hydrocarbon condensate passes to further treatment or handling and the aqueous condensate to the sour water system.

For further information and process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.19 Primary distillation units

Vacuum Distillation

The atmospheric residue is often passed directly to the preheater of a vacuum distillation column where, to avoid thermal degradation, further fractionation takes place at reduced pressure. This is a key step in the upgrading of residue streams and products from vacuum distillation provide important feeds for crackers, lube oil, petroleum coke and bitumen production and heavy fuel oil. Residue from vacuum distillation is a heavy hydrocarbon stream which may be suitable for bitumen production but is often disposed of into the refinery residual fuel oil pool.

Overheads from the vacuum distillation columns, which may contain hydrogen sulphide and organic sulphur compounds, are similarly condensed. Incondensibles pass to vacuum raising equipment (normally staged steam ejectors with indirect condensers). Ejector condensate passes to a barometric sump where incondensibles are extracted to pass either to the process heater for burning or (after compression) to refinery fuel gas. Sour water from the barometric sump passes to the sour water system.

For further information and process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.19 Primary distillation units

1.7.2.3 Hydrogen consuming processes

When subject to catalytic reaction with hydrogen, hydrocarbon fractions undergo a number of reactions according to the nature of the catalyst and the severity of conditions. These processes are principally used to lower the sulphur content of streams to meet end product specifications, by its conversion to hydrogen sulphide, which is readily removable. In the process other impurities may also be removed, eg organic nitrogen and oxygen. Olefins may also be saturated and some cracking may occur.

Relatively mild conditions (1500-7000 kPa, 250-400°C) are used in hydrofining processes to treat light distillate fractions, naphthas to gas oils, to remove bound sulphur, nitrogen and oxygen. On product streams this is to meet quality specifications (eg naphthas, kerosenes, jet fuels, diesel, gas and lube oils). A deeper degree of desulphurisation is becoming necessary to achieve clean product specifications and this typically requires some modification to the process. On intermediate streams, for example feeds to catalytic reformers, the main function is to protect against catalyst poisoning.

More severe conditions (14500 kPa, 350°C) are used in hydrocracking processes where, additionally, cracking of heavier fractions takes place with saturation of olefins and isomerisation. The latter processes are used to up-grade heavy distillates or cracked cycle oils to produce higher value motor gasolines, jet fuel and gas oils.

The most severe conditions (19000 kPa and 350°C) are used in hydrocracking distillation residues (residfining), mainly for up-grading these fractions as flied stocks to catalytic cracking units. These processes have been growing in importance and throughput in response to product demand and specification changes.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.13 Hydrogen consuming processes

1.7.2.4 Gasoline Production Processes

Catalytic reforming

In catalytic reformers, sometimes known as platformers or powerformers, naphthas are up-graded to motor gasoline blending components of improved performance (octane rating). In the process naphthenes are dehydrogenated to aromatics, straight chain paraffins are isomerised to branched chain paraffins, and straight chain paraffins can cyclise to naphthenes. Some hydrocracking also takes place. The overall reaction is endothermic and it is necessary to stage the reactor section and provide interstage heating. A platinum/alumina type catalyst is used, in fixed or moving beds.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.6 Catalytic Reforming

Fluidised catalytic cracking

Fluidised catalytic cracking is an important refinery process in which long chain hydrocarbon oils are cracked to produce gas, LPG and blend components for gasoline, gas oil and fuel oil. It is a very flexible way of upgrading heavy feedstocks into a number of valuable light products and is carried out using continuous processing on a fluidised catalytic cracking unit (FCCU).

The process is also a means of removing sulphur, including sulphur bound in hydrocarbons. Typically up to 50% of feed sulphur is converted to hydrogen sulphide, about 5% to oxides of sulphur and the remainder appears as sulphur compounds in liquid product streams. Refineries are increasingly tending to provide more FCCU feedstock by hydrotreating heavy residues first in dedicated residfiners and also by buying in feedstocks.

The catalyst normally used in the hot fluidised bed is a synthetic zeolite (silica-alumina) substrate carrying rare earth and/or precious metal elements. The active sites of the catalyst are acidic and sensitive to poisoning by heavy metals. The selection of feed streams is therefore important and the tendency to heavier feedstocks is being made possible by advances in catalysts which are improving product yield and quality, while also resisting poisoning.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.5 Catalytic Cracking

Hydrogen fluoride alkylation

This process uses anhydrous, liquid hydrogen fluoride to catalyse the addition of iso–butane to a butylene or propylene molecule. The reaction proceeds at moderate temperatures and pressures and an alkylate (2:2:3 tri-methyl pentane) is formed having a high octane number which is valuable in petrol blending.

Due to the potential problems with hydrogen fluoride, such units tend to be segregated from the mainstream refinery operations, ie have their own independent and integral cooling systems.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.2 Alkylation

Isomerisation

Isomerisation involves converting low octane virgin naphtha, typically containing normal butanes, pentanes and hexane (ie straight chain molecules) to their high octane isomers (ie branched chain molecules). The product is used for blending into the motor gasoline pool and is particularly important in the production of unleaded gasolines.

For further information and process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.14 Isomerisation

Catalytic polymerisation

This is a process whereby unsaturated hydrocarbons, in a mixed feed of saturated and unsaturated hydrocarbons, are polymerised in the liquid phase to produce a high octane polymer gasoline blending component. Feed materials are C3 or C3/C4 streams from units such as the fluid catalytic cracking unit. The by - product is saturated C3 or C3/C4 which is routed downstream for final processing.

The catalyst is a calcined composite of phosphoric acid on a kieselguhr base (known as SPA - solid phosphoric acid) which has an optimum water content for prolonged life and maximum activity. The catalyst is not regenerable but its life is prolonged by hydration of the feed.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.18 Polymerisation

Aromatics production

In this process solvent extraction is used to produce a concentrated aromatics stream from suitable C5-C8 feedstocks, eg reformate from catalytic reforming and imported pyrolysis gasoline. Products may be further processed, eg by hydrodealkylation, to produce benzene.

The solvent used is sulpholane a cyclic C4 compound of high thermal stability which is selective to aromatic compounds. Aromatics are recovered from the solution, and solvent is re-cycled; the non-aromatics are separated as gasoline blending product

For further information and Process description refer to IPPC Reference Document on Best Available Techniques in the Large Scale Organic Chemical Industry February 2003, Chapter 8: Illustrative Processes - Aromatics

Etherification

To improve the octane number of unleaded gasoline, a range of high octane blending components are added. Frequently ethers are used for this, eg methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME). They are mainly imported but some refineries produce them by the etherification of appropriate feedstocks. MTBE and TAME are made from FCCU streams and methanol; another ether, dimethyl ether (DME), an aerosol propellant, is produced directly from methanol. The processes are similar and each uses an etherification reaction in the presence of a catalyst. Feedstock preparation, product separation by fractionation and methanol recovery are also typically involved.

For further information and process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.11 Etherification

1.7.2.5 LPG Recovery and Sweetening

Liquefied petroleum gas (LPG) production

Low boiling hydrocarbons are usually treated in a common plant operating at elevated pressures. The products of this are a desulphurised gas stream (C1 and C2) for sale or use as refinery fuel gas, LPG (propane and butane) and a light gasoline (C5 and higher) stream.

Feedstocks are derived from crude distillation and many other fractionation and conversion operations described in this Note. Pretreatment of some feedstocks may be necessary, typically by hydro-desulphurisation or amine treating.

LPG separation and recovery are normally achieved by cold distillation under pressure using cryogenic cooling systems to maximise process efficiency.

Use of an efficient LPG process can be an important feature in minimising the quantity of gas passing to flare, ie by extracting LPG from appropriate gas streams.

Process description (see Figure 5)

A typical cryogenic process uses propane refrigeration and therefore it is essential to pre-dry the feed streams, which are pressurised and passed through molecular sieve dryers. These are regenerated using hot fuel gas vented to fuel gas or flare.

The feed stream is then cooled and chilled, the residual vapour phase from this being routed to a refrigerated absorber, meeting chilled re-cycled light gasoline absorbent. Absorber overheads (C1, C2) pass to the refinery fuel gas system or may be sold as a petrochemical feedstock. The bottoms are combined with the liquid stream from chilling and pass to the first fractionator or de-ethaniser.

The first fractionator overheads (essentially C2-ethane) are combined with the absorber overheads while the bottoms pass to the second fractionator to produce a C3/C4 overheads stream and debutanised gasoline bottoms.

This overheads stream is routed to a third fractionator to split the C3 and C4 streams as overheads (propane) and bottoms (butane) respectively. Products pass to pressurised storage via any final sweetening by selective molecular sieve adsorption. Subsequent loading of transport containers is carried out by means such as closed loop systems or by venting and release to the fuel gas system.

The gasoline bottoms stream passes to a fourth fractionator to produce a depentanised fraction for use as chilled, re-cycle gasoline on the absorber. The net output is then recombined to form the gasoline product and is routed to storage.

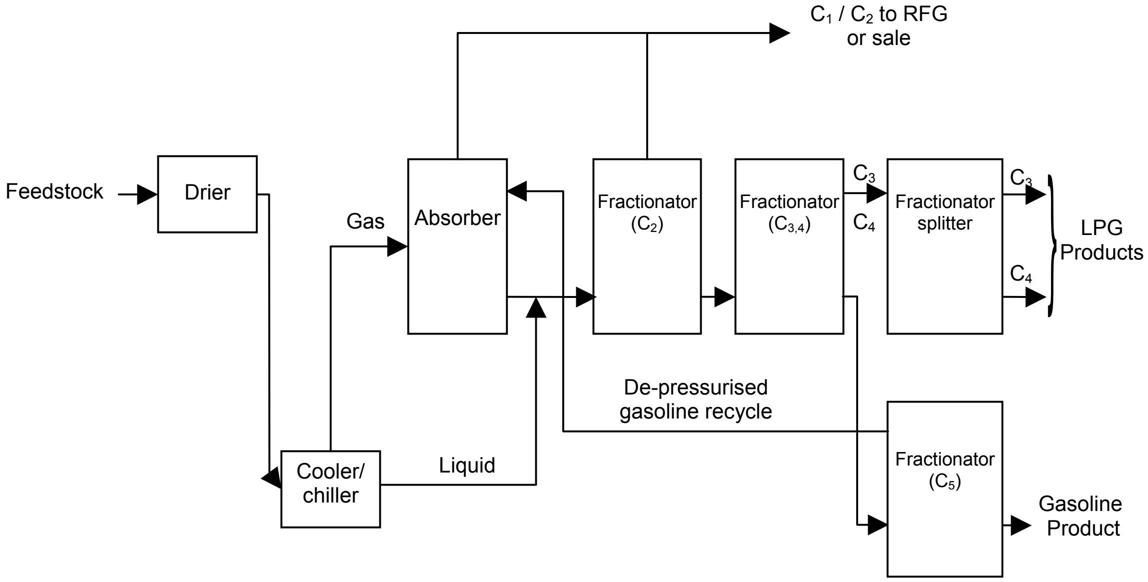

FIGURE 5: LPG PRODUCTION

Chemical treatment (sweetening) processes

To meet quality specifications it is often necessary to sweeten petroleum products and intermediates by removing or modifying remaining sulphur compounds. Sweetening processes are used to convert, and in some cases extract, remnants of hydrogen sulphide and other odorous sulphur compounds, eg mercaptans, from liquid products.

A large refinery typically has several sweetening units on different streams. The mercaptans are oxidised into disulphides, which are stable and not very odorous. From some streams the disulphides are then extracted, eg from LPG or light naphtha, but in most cases they remain with the product.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.20 Product treatments

1.7.2.6 Bottom Barrel Processes and Lubes

Visbreaking (mild thermal cracking)

In this process, so called because it reduces viscosity, oil is heated to above its decomposition temperature. The hydrocarbon molecules break up by thermal cracking to give mixed products, typically fuel gas, visbreaker naphtha and visbroken gas and fuel oils.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.22 Visbreaking

Petroleum coke production

Petroleum coke is currently produced in one UK refinery only and this section is necessarily specific. The process involves a severe and prolonged form of thermal cracking of the pre-fractionated feedstocks and also gives distillates, gas oil and hydrocarbon gases as by-products.

Two types of coke are produced, premium and regular, essentially from two feedstocks -thermal tar from thermal cracking and vacuum residues from vacuum distillation respectively. The process sequence is semi-batch, using a continuous feed to a battery of coking drums yielding 'green coke' which is then rotary kiln calcined, removing any volatile components and producing either regular or premium coke as product.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.7 Coking Processes

Bitumen production

Bitumen is the residue derived from certain crude oils, mainly from the Middle East or South America, after vacuum distillation has removed waxy distillates.

Bitumens are characterised by their softening point and their penetration value. The desired properties may be achieved either by adjusting distillation conditions or by "blowing". In the latter process, air is blown into hot bitumen causing dehydrogenation and polymerisation reactions and giving a harder, higher softening point product.

The main pollution problems with bitumen production relate to hydrogen sulphide releases from the distilled residues and sour condensates and gas produced in the blowing process.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.4 Bitumen Production

Lubricating oil production

Lubricating oils are manufactured at some refineries and are derived from long chain paraffinic hydrocarbons. Feedstocks are waxy distillate side streams from vacuum distillation units or the extract from propane de-asphalting units. Aromatics are first removed by solvent extraction using solvents such as furfural, phenol, n-methyl pyrrolidone and liquid sulphur dioxide. The base lubricating oil is dewaxed by dilution with solvents and chilling. The dewaxed oil is then subjected to mild hydrofining treatment to improve colour and stability.

For further information and Process description refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.3 Base Oil ProductionAncilliary Processes

Hydrogen Plant

For information and process description on hydrogen production refer to IPPC Reference Document on Best Available Techniques for Mineral Oil and Gas Refineries February 2003, Section 2.14 Hydrogen production

Odorising of natural gas or LPG

Both natural gas and LPG are normally given a distinctive smell by the addition of a powerful odorant at a low concentration. The odorants used are typically volatile organic sulphur compounds, ie mercaptans such as ethyl mercaptan and sulphides such as diethyl sulphide. Natural gas is odorised following its refining whilst LPG is normally odorised prior to export from a refinery.

It is an operating requirement that supplied, transmitted or distributed gas has an odour intensity of two olfactory degrees on the "Sales Scale" at a gas concentration of 1% gas in air. Gas is normally odorised immediately prior to entering the national supply system.

Oil industry policy is similarly to odorise LPG to give a distinctive odour at a concentration in air of 20% of the LEL and this may be carried out in bulk storage or as it is loaded into delivery tankers. The odorising process is sometimes known as "stenching".

Process description

Odorant addition to natural gas

For large installations, eg on the main gas transmission system, the liquid odorant is normally stored in fixed tanks, while mobile skid-mounted tanks may be used for smaller duties. The tanks are designed to operate at ambient temperatures ranging from -20°C to +50°C. The liquid is stored under a blanket gas of nitrogen or natural gas and the tank is fitted with emergency relief, venting and vacuum relief systems. The tank is arranged to provide gravity feed to intermediate dosing storage tanks and from these to the injection pumps. The plant is designed to inject continuously, at a controlled rate, liquid odorant into a gas stream at a pressure of normally 7000kPa but it can be up to 9900kPa. The rate of addition of odorant is proportional to the gas flow. Its concentration in the final gas is monitored and this figure is used together with the gas flow rate to determine the rate of odorant addition

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Odorant addition to LPG

The odorant is stored as for a natural gas site. The odorant is not added to the gas stream prior to liquefaction but is usually added to the LPG whilst the LPG is being loaded into the delivery tankers, although in-tank odorising is also carried out. Allowance may be made for any residual mercaptans already present in the LPG. The pump addition rate is carefully controlled. Calibration pots are used to check the rate of addition several times per day and samples are taken to check the level of odorant addition. Normal mercaptan levels for propane are 10-50ppm and for butane 10-40ppm. The rate of injection of ethyl mercaptan is approximately 0.014litre/1000litres LPG.

In the case of liquid propane, methanol may be added with the odorising agent at a maximum rate of 1.25litres/1000 litres of liquid propane, in order to prevent hydrate icing in propane evaporators.

Sour water stripping

Sour water stripping (SWS) is an important part of a refinery's strategy for preventing or minimising releases, both to air and water. Fugitive sour odour problems can be successfully overcome and effluent treatment performance much enhanced by well designed and managed SWS.

Sour water contains hydrogen sulphide and/or low molecular weight mercaptans; it is normally odorous and even small quantities entering the refinery effluent system can lead to severe effluent treatment problems. Hydrogen sulphide emanates from the distillation of crude oils, cracking processes and hydrotreating units, and it is the aqueous condensates from these processes which are the principal sources of sour water. Other sources include neutralisation of spent caustic and flare water seals when sour gas is flared in an emergency.

Sour water can also contain significant levels of ammonia, phenols and cyanides. The composition of this stream varies considerably, depending on refinery configuration and types(s) of crude oils processed. A typical composition is 900mg/l of hydrogen sulphide, 2000mg/l ammonia, 200mg/l phenols and 15mg/l hydrogen cyanide. Sour water streams are collected in enclosed systems and fed to steam strippers to remove these noxious substances.

Stripping difficulty is influenced by phenol and cyanide content of streams, since these species bind strongly to ammonia and hydrogen sulphide; thus sour water from FCCUs is normally more difficult to strip thoroughly than that from hydrotreatment processes.

Process description (see Figure 6)

Sour water is collected from the various sources into a feed drum with separating facilities for hydrocarbons and sour gas which passes to amine scrubbing. Sour water is pumped to the top of the stripper which can be either a packed tower or a trayed column. Steam is injected into the bottom of the tower or alternatively the tower may be fitted with a steam heated reboiler. Overheads are condensed with the condensates being returned as reflux to the column; the gas typically consists of up to 33% hydrogen sulphide and 33% ammonia, with the remainder as water vapour, but composition varies with refinery configuration and stripping duty. It is normally routed to the sulphur recovery units.

Sour water strippers are normally operated as common facilities serving a number of processes and are typically located close to amine scrubbers and/or sulphur recovery units. However some processes may justify individual local strippers to meet their particular needs. Temporary storage of sour water in enclosed tanks may be provided as a buffer during outage of strippers or associated plants.

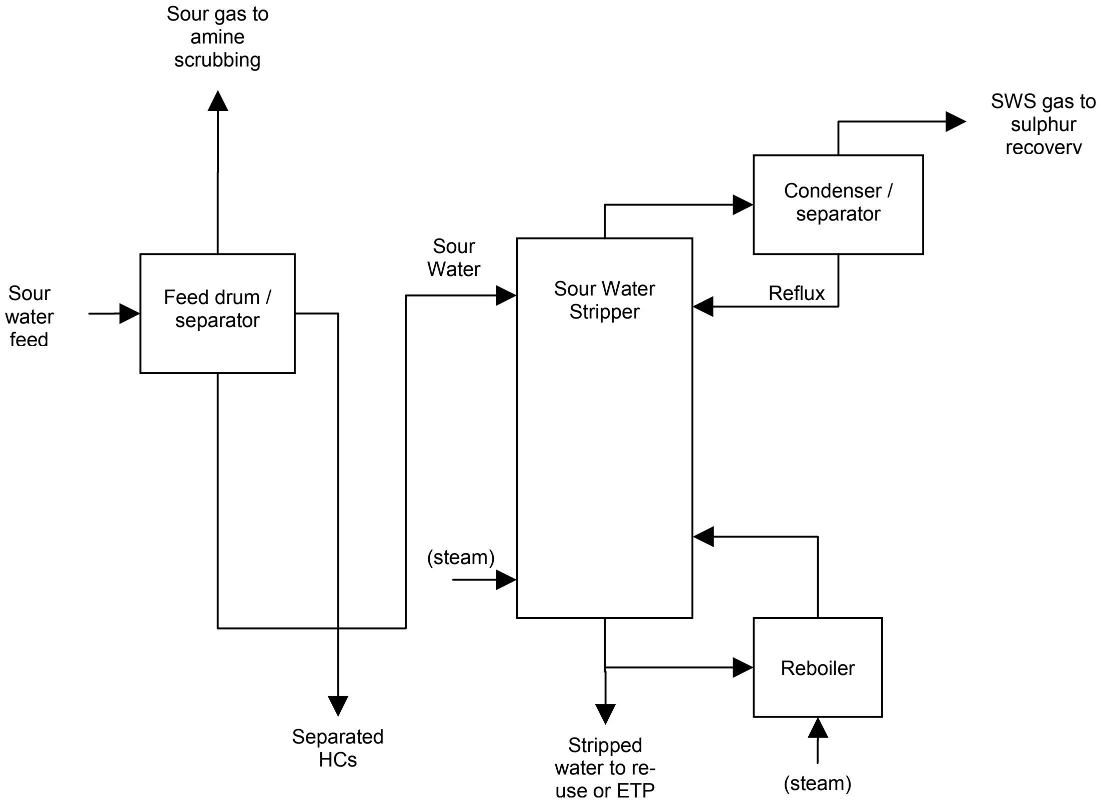

FIGURE 6: SOUR WATER STRIPPING

Sulphur recovery

Sulphur recovery systems are used on all major refineries as the means by which sulphur separated from product streams is captured and converted to a saleable by-product instead of being released into the environment, mainly as sulphur dioxide, either directly from refinery processes or from the subsequent combustion of products, particularly middle distillates and heavy oils. The refinery sulphur balance is discussed in Section 2.1.3.7

Gaseous overhead streams rich in hydrogen sulphide are produced by distillation, hydrodesulphurisation and cracking operations as well as by sour water stripping. Many of these are valuable fuel gas streams which once cleaned can provide a significant part of the refinery base energy requirements as described in Section 1.7.5.1.

Removal is normally carried out in amine scrubbers where an alkanolamine, such as monoethanolamine, diethanolamine or di-isopropanolamine, contacts the sour gas and absorbs hydrogen sulphide which is recovered as acid gas, and is then passed to the sulphur recovery unit(s) (SRUs). The amines are frequently used in specially manufactured proprietary forms chosen to suit the specific application and which may be selective. For example methyl diethanolamine and diglycolamine absorb hydrogen sulphide preferentially to carbon dioxide. The sour water stripper overheads gas stream described above is normally also sent to the SRUs to recover the sulphur and destroy the ammonia. Some units also receive off-gases from petrochemical cracking processes.

The process used almost universally for acid gas SRUs on refineries is the modified Claus process in which high temperature oxidation is followed by catalytic reaction to convert hydrogen sulphide to sulphur, which is normally stored and exported in liquid form. This process typically operates on acid gas streams containing 15-100% hydrogen sulphide. For smaller sulphur recovery duties on acid gas with less than 15% hydrogen sulphide, alternative processes are available, including selective catalytic oxidation and liquid phase techniques such as iron redox or phosphate based processes.

Process description (see Figure 7)

The sour gas meets lean amine in trayed column scrubbers which are adjacent to the hydrogen sulphide sources in most refineries. Overheads sweet gas is routed to the refinery fuel gas system or local use. Rich amine solution is passed to amine regenerators adjacent to SRUs via a feed drum which also separates out any entrained hydrocarbons. Heat is applied via a steam heated reboiler to drive off the hydrogen sulphide as a rich acid gas, normally greater than 90% hydrogen sulphide, which is passed to the SRUs. The lean amine is drawn off the reboiler for re-cycling via buffer storage.

Carbon dioxide may be present in significant proportions in individual sour gas streams and this will be absorbed and transferred by typical amines to the acid gas stream, possibly causing some dilution.

The sulphur recovery process typically consists of a high temperature furnace in which a closely controlled proportion of the hydrogen sulphide is oxidised to sulphur dioxide, followed by a lower temperature staged catalytic reaction of the remaining hydrogen sulphide with the sulphur dioxide to yield elemental sulphur. This process has been extensively developed and improved into many design variants in order to obtain high sulphur recovery efficiency and optimise other process parameters. The basic process is described here with some comments on variations:

In a typical modified Claus sulphur recovery unit with a furnace and three catalytic stages, the main acid gas stream is burnt with a well controlled ratio of air in a furnace according to the equilibrium reactions given below:

$$2H_2S + 30_2 \rightarrow 2S0_2 + 2H_20$$

Unreacted hydrogen sulphide then combines with the sulphur dioxide from (a), as follows:

$$2H_2S + S0_2 \rightarrow 2H_20 + 3S$$

Both reactions occur in the combustion stage, following which heat is recovered by raising steam and the product gases are cooled to condense and remove sulphur. This drives further reaction (b) to the right and is repeated after each subsequent reaction stage.

The sour water stripper gas stream which is routed to most refinery SRUs is typically burnt in the front, i.e. hottest, part of the furnace to maximise ammonia destruction, while the acid gas entry may be split. Furnace design is important and has been optimised extensively by the suppliers with specific features to suit individual situations of gas flows and compositions.

A small sidestream of acid gas is then usually added and burnt in a reheater and the mixture passed to the first catalytic stage, which contains a fixed bed of alumina, where reaction (b) continues, favoured by the lower temperature. Again this is followed by condensing and reheating. Since the reaction is equilibrium limited, overall conversion of hydrogen sulphide to sulphur depends upon the number of reacting and condensing stages. To achieve acceptable conversion three stages are usually installed in modern plants contained in a common vessel.

Design improvements to the basic process are numerous and include the use of advanced catalysts which promote the selective direct oxidation of hydrogen sulphide to sulphur:

$$2H_2S + 0_2 \rightarrow 2H_20 + 2S$$

This is in fact a "non-Claus" reaction and mixed metal oxide spinels are used as catalysts, normally in the final reactor. Another proven technique is the use of a "sub dew-point" cold layer which is progressively moved through the normal Claus catalyst bed, typically on reactors 2 and 3. Special advanced unsteady-state control technology permits this variant, which gives increased conversion since reaction (b) moves further to the right at lower temperatures. The use of oxygen to enrich or replace air has also been shown to be capable of achieving significant throughput improvements while maintaining, or slightly improving, conversion. Modern plants are very energy efficient, eg net exporters of steam.

A tail gas clean-up process can be used to treat the tail gas from the SRU; many different processes are available which are quite sophisticated in design. A typical process rehydrogenates the sulphur species present in the tail gases back to hydrogen sulphide and absorbs this in a selective solvent for re-cycle to the main process.

Residual sulphur dioxide and any hydrogen sulphide normally pass to a tail gas incineration unit, with gas fuel support, before discharge via a stack. Molten sulphur passes through run-down seal legs from each condenser into a holding pit in which it is usually de-gassed of entrained hydrogen sulphide before passing to heated storage for export.

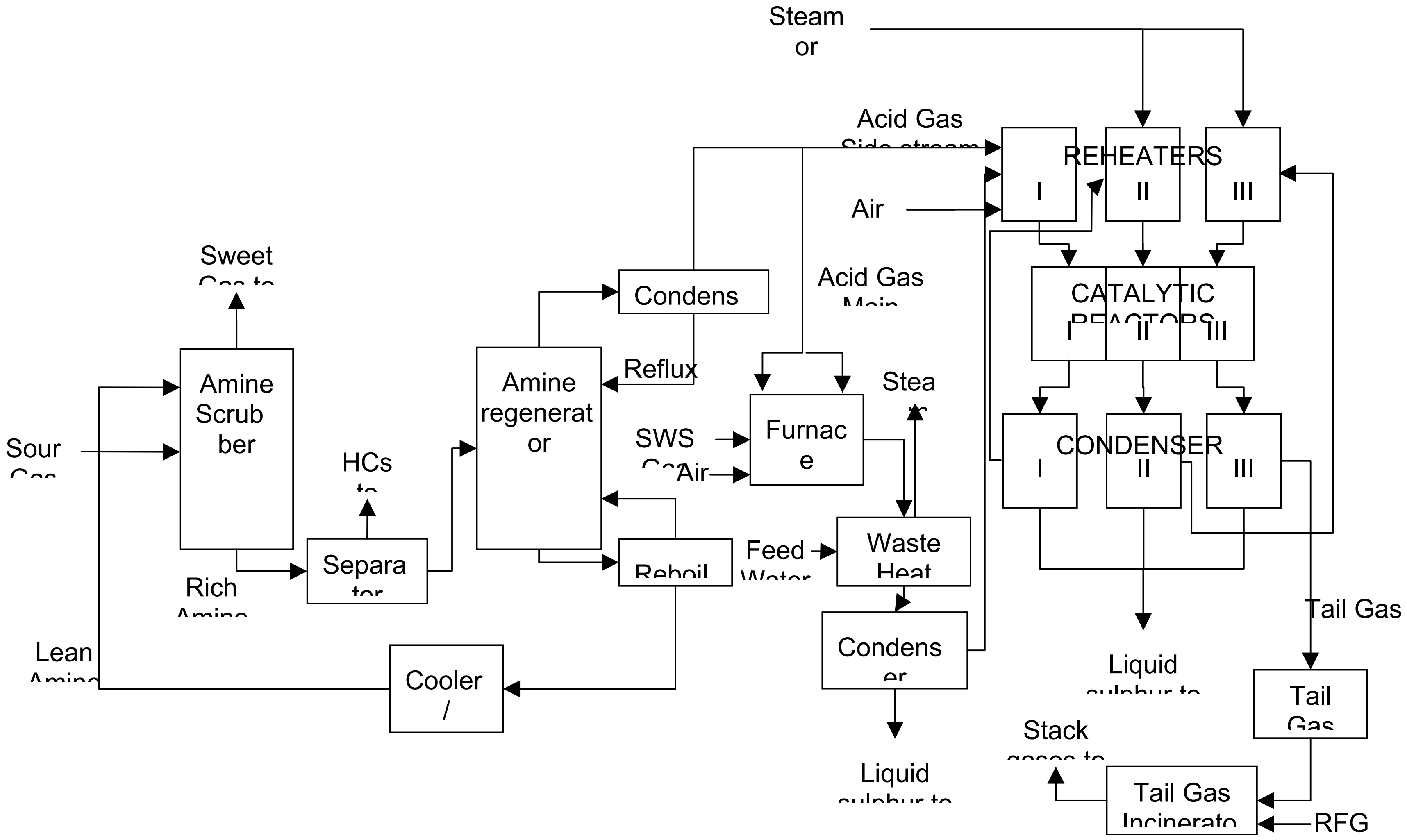

FIGURE 7 : SULPHUR RECOVERY

1.7.3 Natural Gas Refining

Natural gas is collected from gas fields mainly sited off-shore. Before the gas can be transmitted to users the gas is treated and brought up to specification. Gas from the wellheads is collected into a manifold system and piped to a production platform. It is partially treated at this platform and is then transported by pipeline to on-shore gas treatment facilities for final treatment. Chemicals are added to the gas stream either at the well-head or prior to transmission to prevent solid hydrate formation and to limit corrosion in the underwater pipeline. On-shore facilities (terminals) may be connected to several pipelines, each bringing gas in from one or more production fields. The streams are usually kept separate during part or all of their treatment, then metered and mixed together for export.

Natural gas is also obtained from a small number of on-shore oil fields, where it is co-produced with crude oil and separated at local facilities before being treated and brought up to specification and exported.

Most of the gas produced is exported into the national transmission system for supply to users throughout the British Isles and therefore is brought up to British Gas specification; in some cases the customer may be a power generator who requires gas to a slightly different specification, however the same processes are used.

The overall objective of natural gas processing is to remove the treatment chemicals and to remove any contaminants from the well-head stream in order to produce a methane rich gas which satisfies statutory and contractual specifications.

The main contaminants to be removed fall into the following categories:

SOLIDS	Sand
LIQUIDS	Water/Brine Hydrocarbons Chemicals added at well-head
GASES	Acid gases, carbon dioxide, hydrogen sulphide Other gases, e.g. mercaptans, nitrogen

Inspectors should also be aware that naturally occurring radionuclides are present in the fluids produced from some fields. These typically occur as radioisotopes of lead or polonium found as solids in the condensate liquids and although present at low concentrations, they may "plate" out on some processing equipment or be concentrated in deposited scale or sludge. A process may be installed to treat the condensate by deliberately depositing the radionuclides. Some particulate matter filtered out from natural gas may also contain an enhanced level of radionuclides. Depending upon their activity level, the accumulation and disposal of the resulting solids may need to be subject to an authorisation under the Radioactive Substances Act 1993.

Each gas field has a different composition. The gas/water/liquid hydrocarbon ratio and the content of acid gases all vary, depending upon the field. Each well-head in the same production field can also vary and the nature of the gas coming ashore depends upon production rate and the age of the field as well as the type and degree of treatment off-shore.

Most recoverable gas discovered off-shore to the UK has been "sweet", i.e. substantially free from offensive smell due to hydrogen sulphide or other sulphur compounds, typically containing less than 20mg/m^3 of H_2S. However some sour fields are in production and a field can be sweet when first developed but become sour during its lifetime. The potential for change from sweet to sour can be inhibited by the use of suitably chosen biocides which prevent the growth of sulphate reducing organisms.

The gas and main condensate streams are separated in the on-shore slug catcher and the order in which they are treated will vary, dependent upon the level and nature of the contamination and also upon the well-head and on-shore delivery pressures.

1.7.3.1 Off-shore gas handling and on-shore reception

Field operations

Although not subject to Environment Agency regulation, off-shore field operations are briefly described since they determine the gas condition arriving at terminals and therefore the nature and scope of on-shore processes.

The gas can be in contact with brine/water in the reservoir (geological structure containing gas) and a proportion of this liquid is brought to the surface in the well-head stream. This stream can also contain solid material. In normal wells very little solid material is produced but on occasions, mainly due to overflowing of a well from poorly cemented strata, quantities of sand may accompany the fluids from the well-head. The sand drops out in the production separator, which is normally located off-shore.

The gas leaving the production wells is normally saturated with water and can have methanol or monoethylene glycol (MEG) injected at the well-head to reduce hydrate formation during expansion and consequent cooling. The choice of dehydrating agent is often dictated by existing facilities; each has advantages and disadvantages. Methanol is typically used where no off-shore treatment is undertaken. An amine based inhibitor is often injected to reduce corrosion in the well-head riser and other pipelines. Some of the bulk water is removed by gravity at this stage.

On most fields the gas stream is passed to a central processing platform, where the gas and liquid hydrocarbon/water streams are separated in a three phase separation vessel.

The gas phase is dried further in a triethylene glycol (TEG)/water treatment system. It is essential to remove residual TEG from the gas off-shore as it otherwise interferes with the subsequent recovery of any MEG used on-shore. The hydrocarbon liquids together with any free water are pumped to condensate coalescers designed to reduce the water content within the condensate to about 100ppm v/v.

Off-shore gas drying using MEG or TEG normally requires the use of manned production platforms. With the trend to unmanned platforms, new fields coming on-line and existing fields after major re-vamps tend to be bringing relatively wet gas on-shore which requires more extensive drying to meet sales specification. Other drying techniques (eg membrane technology) are being developed which may allow unmanned gas drying off-shore, but they have not yet been proven in practice.

Sea pipeline

Gas is brought on-shore through a pipeline usually laid on the sea bed. New gas fields or production platforms with gas compression facilities can bring well-head gas production ashore as a single dense phase gas. At high pressures (11,000-13,000kPa), the gas and condensate form a single phase system with a density of approximately 300kg/m^3.

As the field depletes, or during times of high demand, the pressure can drop especially in some of the longer sea lines. This can result in liquids settling out in the lower levels of the pipeline and can eventually restrict the gas flow to shore.

In some cases operators can minimise liquid accumulation by managing fields and pipelines in such a way as to create a suitable fluid flow regime, e.g. "mist flow" conditions, under which the gas velocity is high enough to keep liquids continuously dispersed.

Pig/sphere receiver

The maintenance of a pipeline by passing a device through it is known as pigging. In most fields the sea pipeline is pigged to remove any accumulated liquids, using rubber spheres launched from the production platform at regular intervals. Occasionally pipelines are inspected or maintained using a pig specially designed for the function required, e.g. line diameter monitoring. A pig/sphere receiver is used to collect them at the shore end of the sea-line. The receiver is in a direct line with the sea-line and can be isolated from it to allow the spheres or pig to be removed. It may hold a number of devices, e.g. several spheres. This is to reduce the number of occasions the receiver has to be let down to atmospheric pressure to enable the system to be opened. The receiver may be vented down to a low pressure part of the process before it is opened to atmosphere.

Slug catcher

A slug catcher is used to separate the non required liquid fractions (ie hydrocarbon condensate and water) from the gas. The gas/condensate/water is brought ashore at line pressure, varying from around 1000kPa for low pressure sources with most compression on-shore to 13000kPa for high pressure fields. There are two principal designs of slug catchers: oversize pipes or pressure vessels. The gas is free to leave via vertical risers and enter a collecting manifold before being conveyed to the processing area.

The sizing of the slug catcher will normally be based on the gas handling capacity during normal operations but should be able to collect the largest foreseeable liquid capacity from pigging to assist control of the liquid handling plant.

Beyond the slug catcher the process order and detail varies from site to site depending upon the composition of the gas stream and on design choices made for the process. The main typical process operations are shown in
Figure 8 and described below.

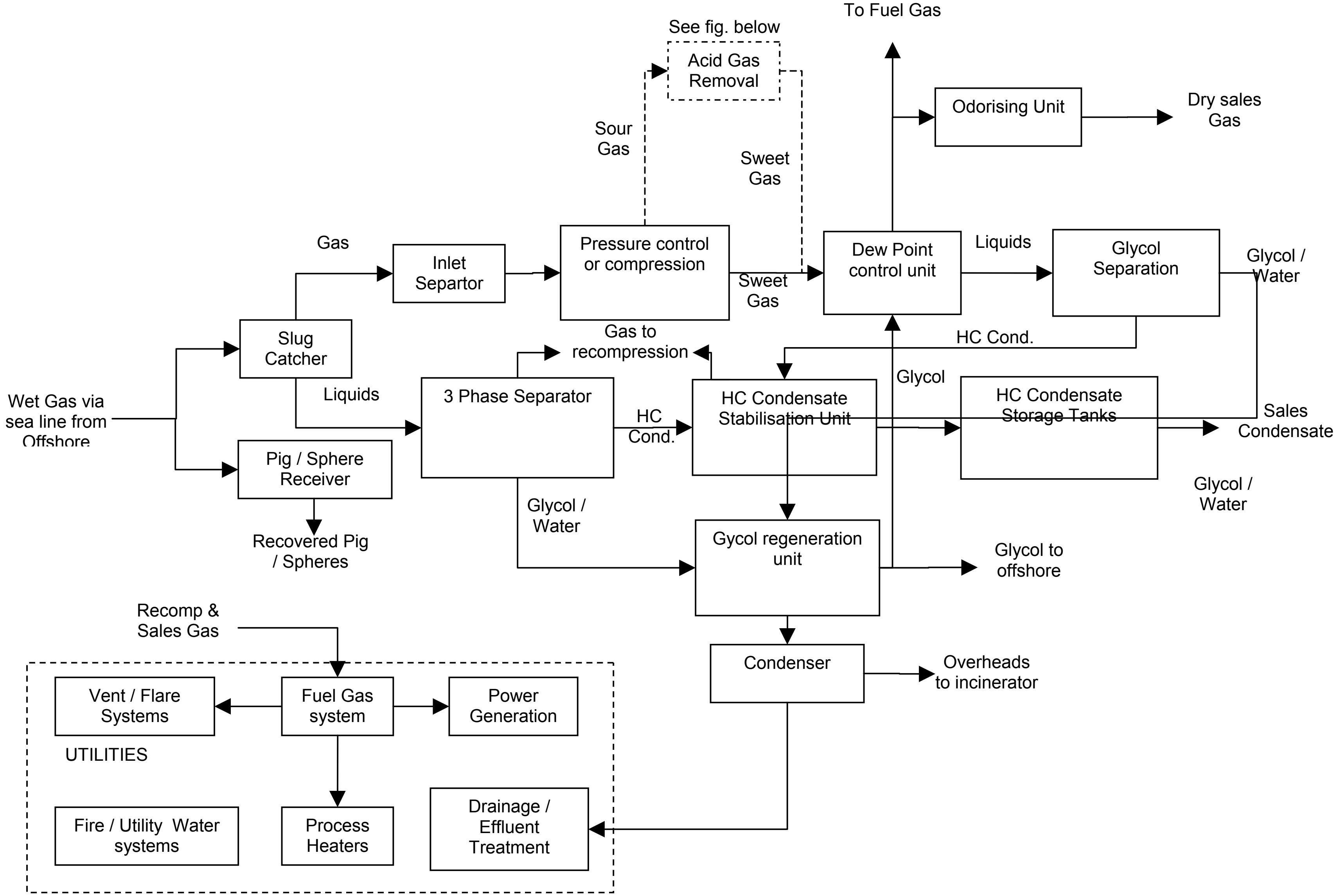
To Fuel Gas
See fig. below
Acid Gas Removal
Odorising Unit
Dry sales Gas
Sour Gas
Sweet Gas
Gas
Inlet Separtor
Pressure control or compression
Sweet Gas
Dew Point control unit
Liquids
Glycol Separation
Glycol / Water
Slug Catcher
Gas to recompression
HC Cond.
Glycol
Wet Gas via sea line from Offshore
Liquids
3 Phase Separator
HC Cond.
HC Condensate Stabilisation Unit
HC Condensate Storage Tanks
Sales Condensate
Pig / Sphere Receiver
Recovered Pig / Spheres
Glycol / Water
Gycol regeneration unit
Glycol / Water
Glycol to offshore
Recomp & Sales Gas
Condenser
Overheads to incinerator
Vent / Flare Systems
Fuel Gas system
Power Generation
UTILITIES
Fire / Utility Water systems
Process Heaters
Drainage / Effluent Treatment

FIGURE 8: SIMPLIFIED TYPICAL ONSHORE TREATMENT PROCESS (WET GAS/GLYCOL PROCESS)

1.7.3.2 On-shore gas treatment and liquid removal

Before all the water has been removed from the gas stream and whenever the pressure or temperature of the gas stream is reduced, there should be a system to prevent hydrate formation and consequent icing.

Inlet separators

After leaving the slug catcher, the pressure of gas from high pressure fields is reduced to the inlet separators which are slightly above the grid distribution pressure of 6800-7100kPa (up to 7600kPa if uprated). The separators usually contain vane elements to aid coalescence of liquids and the recovered condensate is returned to the condensate stabilisation system. They may also include filters to remove particulates and may be followed by suction scrubbers if on-shore compressors are needed to bring low pressure gas up to sales pressure. Further processing of the gas then takes place at this pressure. With high pressure fields, the gas chills as the pressure is reduced and this cooling effect can be utilised as part of dew-point control.

Gas dew-point control

If the gas contains hydrocarbons heavier than methane, the dew-points are usually achieved by using a refrigerant system to cool the gas and remove any condensed liquids including condensate and water/glycol. These liquids are separated in the low temperature separator after the chiller to be treated in the condensate stabilisation plant and glycol regeneration respectively. Counter current gas/gas heat exchangers in series are used to pre-chill the feed gas and simultaneously reheat the exit stream after chilling; glycol is spray injected at successive points between the tube plate headers. If on leaving the heat exchanger the exit gas is still too cold for transmission down the grid system, it is heated in a separate hot oil heater or similar system. It is possible to achieve this heating in an energy -efficient manner, e.g. by heat exchange with the hot part of the refrigerant circuit.

Dew-point control using molecular sieve or silica gel systems

Molecular sieves or silica gel can also be used to dry the gas prior to distribution. The water and hydrocarbons are adsorbed on to a packed bed of adsorbent. The bed is regenerated using a hot gas stream (usually re-cycled dried gas) which is then cooled below the dew point so that the condensate/water drops out. The liquids are phase separated and sent for recovery. The drying gas is returned to process and any flash gas from the condensate knock-out pot is flared or returned to the system. Such systems offer economic and environmental benefits compared to refrigeration and should be considered as options for new dew-point control processes.

From some fields gas may contain liquefied petroleum gas (LPG) or nitrogen and hence require low temperature separation to remove these contaminants. As a result, the level of water remaining in the gas from a plant using a glycol de-watering system causes problems with blockages in the liquefied petroleum gas removal train. In these cases molecular sieves or silica gel should be used. The molecular sieve can be designed to operate with sour gas. In some fields it is used to de-water and clean the gas/condensate as a single dense phase gas and therefore reduce the number of treatment plants on site. Alternatively, where relatively dry dense phase gas is brought on-shore, TEG may be used at a low ratio to remove residual water down to a very low level before the gas enters the LPG train.

Dew-point control using pressure reduction

For gas that is brought on-shore at high pressure, e.g. dense phase gas, which has to be let down to the grid distribution pressure, it is possible to use carefully designed pressure reduction to provide dew-point control through adiabatic cooling. This may be achieved by means of a Joule-Thomson valve followed by separation of liquids and gas reheating as necessary. Alternatively, use of a turbo-expander enables energy to be recovered as part of this stage.

Liquid removal

The liquids that collect in the slug catcher require separation into the hydrocarbon condensate and water/methanol or water/glycol phases. In some cases this is achieved by careful density monitoring of liquid batches pumped from the slug catcher and diverting the flow when the phase change is detected. Preferably the combined liquids from the slug catcher flow to a three phase separator from which the two liquid phases are taken for treatment. On some fields the operator may elect not to process the liquids further. Instead they are pumped back off-shore for re-injection into wells or possibly on gas/oil coproduction fields, mixed with crude oil product.

Glycol regeneration unit

The liquid recovered in the dew point control plant is passed to a three phase separator and the glycol rich layer goes to the glycol regeneration unit for distillation. Water dissolved in the glycol is vaporised and removed in the steam overheads from the still, leaving regenerated glycol, usually 75-80%w/w, to be cooled and stored for re-use. The steam carries with it small but significant amounts of hydrocarbons, aromatic compounds, MEG, plus carbon dioxide and sulphur compounds if these are present in the gas stream at dew point control.

The steam is normally condensed to reduce releases to air and avoid a visible atmospheric emission plume and this produces a highly contaminated liquid effluent, although fairly small in volume terms (typically less than 200litres/hour). It has a high biological and chemical oxygen demand value due to the contamination with MEG and other organic compounds. It can also be very odorous if a sour gas field is being treated and sour water stripping may be needed to pre-treat the liquid stream before further treatment. Any residual vapour phase overheads and off-gas from sour water stripping should pass to an incinerator. The liquid effluent stream should be treated to reduce its organic content and oxygen demand before being allowed to mix with other aqueous discharges in the process drainage system.

Occasionally gas may be brought on-shore that contains appreciable amounts of brine, e.g. as a field depletes and gas/briny water interface rises. This can lead to salt dissolving in the glycol and the concentration rising to saturation point as the glycol inventory constantly recycles. The consequent deposition of solid salt will then give serious operating problems, e.g. in the dew-point control process where the glycol is atomised into a fine spray. In these circumstances it is necessary to remove a bleed of salt to maintain its concentration below the saturation point. This can be done off-site or if justified by the scale/duration of the problem, an evaporative desalination process may be installed within the glycol unit. Calcium salts may also build up and require to be precipitated as part of the process. The separated solids are disposed of off-site.

Where TEG is used for final deep dehydration prior to LPG trains, regeneration normally involves specialised low temperature distillation or stripping processes that prevent TEG degrading; it is possible by careful design to produce an off-gas containing the water vapour and sufficient C1- C4 hydrocarbons such that it can be used (with support) as fuel gas and hence avoid generating a liquid effluent.

Methanol regeneration unit

Gas which has not been partially dried off-shore may contain about 2 barrels of water/100ft^3 of gas (11.2litre water/1000m^3 gas). On-shore, most of the water and the methanol added off-shore will separate out in the slug catcher with the condensate, although some enters the gas phase. The methanol/water mixture is distilled and the methanol taken off as vapour and condensed for return by pipeline to the well-head. The bottoms liquid contains the water together with residual methanol and traces of hydrocarbons and other chemicals, e.g. corrosion inhibitors. This liquid effluent will need treatment to remove the contaminants before release to controlled waters, either on-site or by discharge to a sewer for treatment elsewhere. Any brine contained with the water will also enter the liquid effluent.

Acid gas treatment

Introduction

The acid gases commonly associated with natural gas reserves are carbon dioxide and hydrogen sulphide. The method of removal chosen depends to a large extent upon their concentrations, but also on the relative levels of each acid gas, and the proportions of each that need to be removed to meet the sales gas specification.

Acid gas removal - high concentrations

For the removal of acid gases at percentage levels, the normal system of treatment is based upon absorption of the gas into a suitable physically or chemically reactive solvent. This is then regenerated by a combination of heating and pressure reduction. The waste gas stream evolved from the regeneration is collected and treated.

There are many processes licensed for acid gas removal based upon these general principles, but this Note only describes general process types. Although the operator may have a clear preference for a particular solution, the alternatives considered should be presented in the application in sufficient detail for the Inspector to be able to validate the chosen solution as BAT.

Amine processes

Alkanolamines, notably monoethanolamine and diethanolamine, are the most widely used solvents for the removal of hydrogen sulphide and carbon dioxide from natural gas streams. The amines are frequently used in specially manufactured proprietary forms chosen to suit the specific application; these are often chosen to be selective,

e.g. to absorb hydrogen sulphide preferentially to carbon dioxide. Methyl diethanolamine is an example of this. They are normally used in aqueous solution and sometimes a combination of amines is employed. It is important to remove any contaminants, e.g. solid particulates or liquids, before contacting sour gas streams with amines as extensive foaming can occur if dirty gas is treated. A typical process is shown in
Figure 9.

Carbonate processes

The hot potassium carbonate process requires a relatively high partial pressure of carbon dioxide to operate efficiently. The high processing pressures of natural gas treatment tend to give relatively high acid gas partial pressures and have resulted in the process being regarded as economical for the sweetening of natural gas with medium to high acid gas contents. Process flow is similar to the amine process described above. Carbonate processing can be used in combination with ethanolamines.

Solvent processes

There are many different licensed physical solvent absorption processes available, and they are also similar in nature to the amine process. The solvents include water, methyl cyanoacetate, glutaronitrile, ethylene cyanohydrin, propylene carbonate, ether compounds of diethylene glycol and sulpholane. Processes are also available that use a combination of physical and chemical solvents.

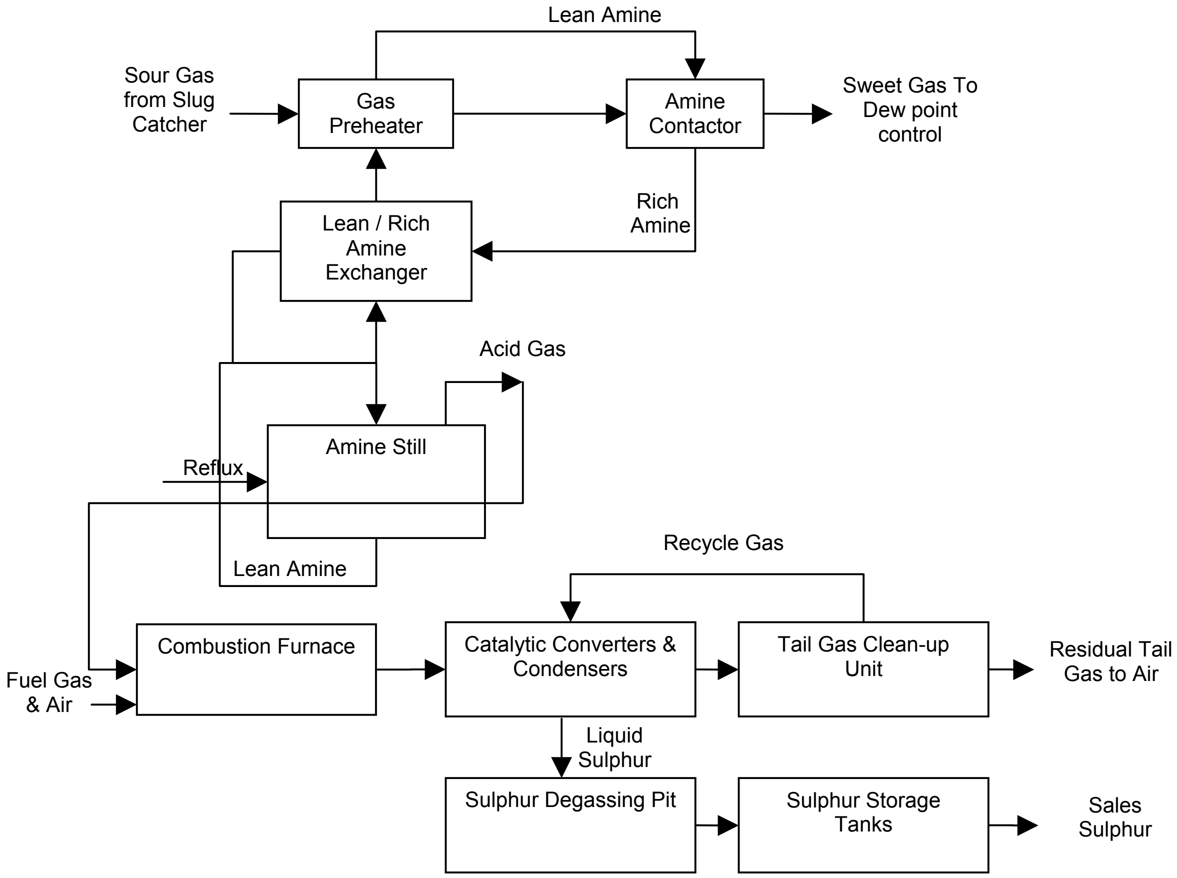

FIGURE 9: SIMPLIFIED TYPICAL ACID GAS TREATMENT PROCESS (AMINE/CLAUS PROCESS)

Process choice

At high levels of hydrogen sulphide a physical or chemical absorption process should be used. The regeneration of the solvent allows the hydrogen sulphide released to be at a concentration that makes the adoption of a sulphur recovery process feasible. The choice of solvent absorption process should take into account environmental considerations and energy requirements as well as process suitability and economic factors.

The carbonate process has some advantages over amine processes. It can remove carbon disulphide and carbonyl sulphide without significant solution degradation. The primary difficulty with the process is that it requires the use of vanadium or boron salts to inhibit corrosion. Amines can also be used as activators.

Sulphur recovery

The modified Claus process

This is the process most widely used on high hydrogen sulphide content streams and it will typically operate on gas streams containing 15-100% hydrogen sulphide. The process is described in more detail in section 1.7.5 a simpler overview is given here and in
Figure 9.

The process uses partial thermal oxidation followed by chemical conversion over a catalyst. The acid gas is burnt with a controlled ratio of fuel gas and air in a combustion furnace to oxidise part of the hydrogen sulphide to produce sulphur dioxide. This is reacted with the remaining hydrogen sulphide in a ratio of 2:1 while passing over an alumina catalyst bed to give sulphur which is subsequently condensed and recovered. The catalytic reaction is equilibrium limited and three stages are typically required to achieve acceptable overall sulphur recovery. Any hydrocarbons are oxidised to carbon dioxide and therefore compete for oxygen and need to be minimised in the feed gas. The tail gas from a standard process will normally require further treatment in a tail gas clean-up process. The liquid sulphur product is degassed of any hydrogen sulphide or other gases prior to export.

The residual treated tail gas stream is normally incinerated to convert any remaining hydrogen sulphide and other sulphur compounds to sulphur dioxide before release.

Other processes

Fixed bed selective catalytic oxidation processes are applicable to the range 1-15% hydrogen sulphide and use catalysts based on combining two or more metal oxides, directly to oxidise hydrogen sulphide to elemental sulphur at moderate temperatures. They can give a high recovery efficiency, even in the presence of hydrocarbons and water vapour.

REDOX processes are applicable to gases containing less than 10% of hydrogen sulphide. These are based on catalysts such as iron complexes, anthraquinone or thioarsenic compounds dissolved or suspended in a liquid phase. They are brought into contact with the sour gas in an absorption tower and circulated to a regeneration column where air is blown through the liquid.

These processes are of a simple compact design, have high hydrogen sulphide removal efficiency, are selective and typically have a higher turn down ratio than the Claus process. They can be readily started up or shut down which makes them amenable to cyclic operation or coping with sudden gas demand changes. They also have low energy requirements.

Carbon dioxide-rich gas stream

Where necessary, carbon dioxide content has to be reduced to a level which allows the sales gas to meet a specified "Wobbe Number". This is a measurement of the flame stabilisation characteristics of the gas required to meet specification. However, gas containing higher levels of carbon dioxide may be passed to a utility designed to burn gas at a lower flame stability. A gas turbine designed to operate on such a gas stream would still produce less carbon dioxide/megawatt than a conventional oil or coal burning power station. This gas could also be used in the site fuel gas system.

Acid gases at low concentrations
Low levels of carbon dioxide normally cause no problems. The gas can be blended to achieve, or will already be at, an acceptable flame stability number.

Low gas concentrations of hydrogen sulphide can be removed by adsorption on to a molecular sieve, which can be regenerated using hot process gas. The regenerated gas, which is rich in the contaminant material, can be passed to sulphur recovery as above.

Alternatively the hydrogen sulphide can be directly reacted with a bed of zinc oxide. This process is usually only considered economic for very low concentrations of contamination since it is not locally regenerable. Instead the spent bed is occasionally returned to primary zinc manufacture, where the sulphur is recovered as sulphuric acid by-product, while a fresh bed is installed.

Nitrogen removal
Nitrogen can be present in percentage quantities. Its removal may be necessary to meet the calorific value or flame stability criteria for natural gas and the only suitable process is cryogenic distillation. The gas should be free of water, carbon dioxide, hydrogen sulphide and high molecular weight hydrocarbons before the natural gas stream is liquefied. The "overheads" (incondensibles, including the nitrogen) from the still are discharged to atmosphere; plant design should be such as to ensure that the distillation column is sufficiently effective to reduce the methane content of the overhead stream to an acceptable level or for subsequent treatment before release. Typically the nitrogen is removed from a portion of the gas stream which is then re-blended with main flow after treatment to give sales gas which meets specification.

Hydrocarbon removal
Any hydrocarbon above methane in the series present in the gas phase is removed along with the water in the dew-point control system or molecular sieve processes described above. The liquid hydrocarbons are taken to the condensate stabilisation system. If the gas field contains a high proportion of C2-C4 hydrocarbons these are recovered either as individual products or as one or more product mixtures.

Other gas treatment and ancillary processes
When fully processed the gas may be finally filtered, normally through a fibre glass filtering medium. There may be several of these units operating in parallel to remove dust down to 2μm level. The gas is then odorised to the required level, which is subject to the total sulphur content being not more than 15ppm. This is continuously checked by an odorant chromatograph system before the gas is metered into the national grid system. The odorising of natural gas is described in section 0. In some cases gas may be separately odorised outside the process boundary of the terminal as it enters the transmission grid, e.g. where there are several adjacent terminals.

In some cases, key control valves are actuated by natural gas, e.g. for rapid shutdown safety valves. These usually vent the used gas to atmosphere after operation.

Condensate treatment

A number of condensate treatment processes are used, typical examples of which are described below.

Condensate stabilisation using column process

Stabilisation is the full removal of light fractions from the condensate, usually achieved by pressure reduction and heating. A typical process involves pressure reduction to a stabilisation column, which is normally a bubble cap column, the liquid descending the column under gravity to a reboiler with the column operating under reflux. The fully stabilised bottoms product is cooled, pumped to storage and subsequently transferred by pipeline to a refinery or other process area. Overhead flash gas is recompressed where necessary for use as fuel gas.

Condensate stabilisation using flash process

Flash stabilisation is a simpler process in which condensate is fed to a flash drum where the pressure is let down. The condensate feed is normally preheated, in which case the product is sufficiently stabilised to be passed to stabilised condensate storage. If the feed is not preheated, the product is not fully stabilised and is passed to semi-stabilised condensate storage where it is allowed to weather before export. Flashed off gases are used as fuel gas and a re-run facility may be provided to allow reprocessing if required.

Condensate sweetening

There are numerous licensed processes for the "sweetening" of a liquid condensate. As well as containing dissolved hydrogen sulphide gas the liquids contain naturally occurring mercaptans, carbonyl sulphide and carbon disulphide. These odorous sulphur compounds should be eliminated to enable the product to be handled without causing complaints.

The most common method of treatment is oxidation to disulphides, by a process that involves one of the following methods:

- Homogeneous catalysis - The reaction takes place in a caustic soda solution which is contacted with the hydrocarbon liquid. The caustic stream contains a transitional metal catalyst, such as cobalt, copper etc, in suspension. Air or oxygen is injected into the caustic solution and the sulphur compounds are oxidised through to a disulphide compound which is relatively stable and not very odorous. The caustic solution is gradually replenished as the sulphur compounds etc reduce the pH of the caustic medium.
- Heterogeneous catalysis - The caustic and condensate pass through a solid support material which has been coated with a transition metal catalyst. The catalyst slowly goes into suspension, released by the acidic constituents of the feedstock and the oxidation occurs as above. The fixed bed sweetening systems require occasional addition of caustic to adjust pH and at times the bed has to be removed to recatalyse the support material. This method of treatment is preferred as it reduces the concentration of the metallic catalyst in the caustic soda which has to be disposed of from time to time.

- Metal oxide treatment - The condensate can be treated by passing it through a fixed metal oxide bed, such as zinc oxide.

Condensate storage

Stabilised sweetened condensate is normally stored in floating roof tanks. Semi-stabilised or unsweetened condensate is stored in fixed tanks with a nitrogen or natural gas blanket. The semi-stabilised condensate will release low molecular weight hydrocarbons into the gas space in the storage tank; unsweetened condensate will cause odours. The tank pressure is controlled and any over-pressure is released, preferably to recompression, but alternatively through a small flare system or through an incinerator with support fuel to oxidise any hydrocarbon or sulphur compound releases.

There should be an automatically controlled blanketing system to keep the minimum positive pressure in the tank.

Storage sites on national gas transmission system

There are a small number of gas storage sites located at key points on the national transmission system, storing gas either as liquefied natural gas (LNG) or as compressed gas. LNG is stored in insulated tanks and compressed gas in underground salt caverns and in a depleted off-shore field. These are used as buffer storage to protect the integrity of the transmission system at times of high gas demand and/or supply shortfalls. The process involves the partial refining of gas.

The sites differ somewhat in design and scope with those sites which liquefy and store LNG being the most complex. All the sites need to be independent of other energy sources and are thus equipped with gas or diesel fired electrical generation equipment to cover external power failures. Gas is withdrawn from the high pressure transmission system at times of low demand, stored and then returned to the system to maintain line pressure when demand is high or there is a supply shortfall.

LNG storage

At the LNG sites it is first necessary to remove impurities from the imported gas in order that it can be stored as a liquid. The impurities consist of the odorant contained in the transmitted gas, together with traces of moisture, carbon dioxide and hydrogen sulphide. They are removed by appropriate treatment processes, including selective solvent absorption and adsorption on to beds of molecular sieve and silica gel. These are normally contained in common towers in tandem which are regenerated when saturated using a hot re-cycled dried gas stream. The exit gas stream from the tower being regenerated is either sent to incineration on-site or is fed via a knock-out pot to the local low pressure gas mains for distribution to users.

The refined gas is liquefied by refrigeration using a series of heat exchangers and higher molecular weight hydrocarbons are removed in knock-out pots for re-injection into the local or national transmission system. The LNG passes to the insulated steel storage tanks where its pressure is reduced to just above atmospheric; this further cools the LNG to the storage temperature of -160°C. Some methane and nitrogen are flashed off and are compressed and returned to transmission. Refrigeration is normally achieved by a hydrocarbon system with centrifugal compressors.

When gas is required to be exported to the national transmission system it is vaporised using gas fired units of the submerged combustion or direct fired type and re-odorised before leaving the site.

Compressed gas storage in salt caverns

During stock-building, imported gas is passed through a series of small cyclones to remove any traces of solids and liquids and then compressed to a high pressure before flowing through wells into the underground storage cavities. These are artificial caverns in a thick salt stratum constructed for use as impervious gas reservoirs. Any liquid hydrocarbons removed are stored and disposed of off-site.

When gas is required to be exported, it is put through a partial refining process to remove impurities arising from storage. These include salt particles, brine and hydrocarbon liquids and water vapour. Methanol is first injected at the cavity well-head to suppress hydrate formation during subsequent cooling and the gas is passed through primary and secondary micro-scrubbers which use cyclones and cartridge filters to remove solids and liquids. The gas is heated to allow for the cooling effect as the pressure is reduced back to that of the transmission system and then dried using triethylene glycol absorption or silica gel adsorption. Finally the exported gas is re-odorised to compensate for any odorant lost during storage and processing.

1.7.4 Gasification of Solid and Liquid Feedstocks

Gasification involves the reaction of a source of carbon, possibly with associated combined hydrogen, with a source of hydrogen and/or oxygen to yield a gas containing carbon monoxide, hydrogen, carbon dioxide and methane in proportions dependent on the ratio of the reactants utilised and on the reaction conditions. Water vapour will also be present.

The carbonaceous feedstocks would normally be coal, lignite or liquid hydrocarbons ranging from condensate or light distillates to residual oils or asphalt’s. Other possible feedstocks include bitumen, petroleum coke, waste lubricants, waste plastics and other carbonaceous wastes.

The principal processes available are:

- catalytic gasification with steam;
- thermal hydrogenation; and
- gasification with oxygen and/or steam, or with air and steam.

The feedstock is prepared and fed to the gasifier in either dry or slurried form. The feedstock reacts in the gasifier with steam and oxygen at high temperature and pressure to produce the syngas. Inorganic materials (such as ash and metals) are converted into a vitrified material resembling coarse sand. With some feedstocks, valuable metals are concentrated and recovered for reuse.

The resulting gas may then be desulphurised and particulates removed, leaving a "cleaner" fuel gas for combustion in a conventional gas-fired boiler or more efficiently by using combined cycle gas turbine technology. This latter process is known as

Gasification Combined Cycle (GCC) and various degrees of integration are possible.

With the exception of two installations using Lurgi fixed-bed dry ash gasifiers and a number of small plants using by -product coke as a feedstock, gas production from coal was formerly conducted using variations of the old fashioned gas works and coke oven batteries. These processes were phased out in the late 1960s / early 1970s when cyclic and continuous plants using light distillates became available. The latter were progressively phased out following the introduction of natural gas. It is not expected that partial gasification in batteries would form any part of future plans for coal gasification. Any future coal gasification plants would probably utilise high throughput continuous complete gasification plants or possibly partial gasification plants.

At the present time, there are many proven gasification plants around the world, mainly in the in the chemicals industry or making synthetic transport fuels; global syngas production is growing at around 10% per annum. Consequently, gasification is considered a commercially proven technology.

Commercial processes and those in advanced development

Any solid or liquid feedstock containing carbon can be gasified. The use of oxygen rather than air will produce a gas with a higher heating value and a mix of mainly hydrogen and carbon monoxide, with some methane, depending on the process. The quantity of hydrogen could be increased by further processing through a shift converter.

Oil feedstocks available for large scale commercial gasification can range from natural gas liquids through to high sulphur heavy residual oils from refinery operations. The choice of process used depends on the product required and the composition of the feedstock. For example it may be required that the product is rich in hydrogen and/or carbon monoxide for use as a chemical feedstock (synthesis gas) or rich in methane to facilitate conversion to SNG. Product gas rich in hydrogen would be required for use in hydrogenation reactions.

Processes are also available for the complete or partial gasification of coal. The latter processes are usually part of topping cycles and the residual solid (char) is usually sent forward for combustion in a fluidised bed combustor. One such process, the Air Blown Gasification Cycle (formerly known as the British Coal Topping Cycle), is included in this Note.

Processes which have been operated on a commercial basis include those listed below.

Catalytic gasification with steam

This process can be utilised with distillate oil fractions. Sulphur-free light distillates are reacted with steam over a nickel based catalyst to give a primary gasification product containing methane, carbon dioxide, carbon monoxide and hydrogen.

The proportion of gasification products is dependent on the reaction temperature; higher temperatures are necessary for heavier feedstocks. These result in a reduction of methane and carbon dioxide content and increases in the carbon monoxide and hydrogen concentrations. If the process is being used for SNG production further catalytic methanation stages can be used operating at lower temperatures when the equilibrium moves in favour of methane production. At temperatures of around 300°C a product containing methane and carbon dioxide in the ratio of approximately 3:1 results, with only traces of carbon monoxide and hydrogen remaining. After removal of carbon dioxide the gas is substantially pure methane.

Thermal hydrogenation

The removal of sulphur from heavy fuel oils is more difficult than from distillates. Consequently heavy oils cannot be gasified catalytically with steam because the sulphur content leads to catalyst poisoning. They can however be reacted directly with hydrogen at high temperatures and pressures to make methane, ethane and by-product aromatics. The gas can then be readily desulphurised.

Gasification with oxygen (or air) and/or steam

These gasifiers generally operate at high temperatures. The solid or liquid hydrocarbon feedstocks are reduced to low molecular weight substances such as carbon monoxide and molecular hydrogen. The chemical reactions which take place in these gasifiers are numerous. Essentially in an oxygen and steam fed gasifier the reactions may be summarised as:

$C + H_20 \rightarrow CO + H_2$ steam/carbon reaction, and

$C + {}^1/_2\, 0_2 \rightarrow CO$ partial oxidation.

The composition of the synthetic gas which is produced by the gasifier will depend on the feedstock utilised, the steam to oxygen ratio and the temperature and pressure at which the gasifier is operated. Although oxygen is fed into the gasifier, a reducing atmosphere exists and as a result sulphur present in the feedstocks is converted to H_2S, with smaller amounts of carbonyl sulphide, methyl mercaptan and carbon disulphide being produced.

Fuel-bound nitrogen will be mainly converted to molecular nitrogen, but in the presence of hydrogen, some small quantities of ammonia and hydrogen cyanide will be produced. The ratio of ammonia to hydrogen cyanide is of the order of 100:1.

The nitrogen formed as a by -product of air separation to produce oxygen for the gasifier may be used to provide inert atmospheres in the milling and dust handling areas of coal fed gasifiers and where IGCC plants are operated, it can be fed to the gas turbine to assist in lowering NOx formation and recover power.

Gasifiers can achieve between 70 and 93% cold gas efficiency (most operate at between 78 and 85%) and over 99% carbon conversion can be expected from many gasifier designs where coal or residual oils are the feedstocks. Much of the remaining energy in the feed can be extracted as usable heat. Inspectors should note that cold gas efficiency can be misleading if comparisons are being made between different gasifiers, different feedstocks (fuels), or between gasification and other (e.g. direct combustion) technologies.

Different designs of gasifiers operate at markedly different temperatures. Those operating at lower temperatures will release the mineral content of the feedstock as an ash, which can be separated from the fuel gas stream; whilst those operating at higher temperatures will produce a molten slag which can be quenched in water to produce a hard, generally non-leachable glassy slag.

Some of these processes can produce a significant carbon carryover in the form of soot which can be removed prior to the main product purification stages, e.g. by water wash after gas cooling.

Processes are available for the recovery of the soot from the water wash and this may be recycled to the gasifier with fresh feedstock. Sulphur in the feedstock is present in the crude gas as hydrogen sulphide or carbonyl sulphide and, dependent on the subsequent use of the gas, can be removed to varying extents down to sub ppm levels. The regenerative absorption or chemical methods used for removal of acid gases results in a concentrated acid gas stream which can be treated to produce elemental sulphur.

The conditions reached in these gasifiers, ensure that in well managed systems no polycyclic organic or phenolic materials are present at detectable levels.

Gasifier designs may be divided into three sub-groups:
- entrained flow
- fixed bed
- fluidised bed.

Brief descriptions are given below:

Entrained flow gasifiers

This is the most widely used design type. The reaction takes place in an entrained fluid flow or total suspension. This gasifier can be fed pulverised (-0.1mm) coal (dry or in a slurry) or liquid hydrocarbons. Where coal is the feedstock, oxygen and steam are fed into the gasifier and the maximum operating temperature in the gasifier will normally be 1500 to 1900°C with operating pressures of 25-50bar. With oil feedstocks the operating range is 1300-1500°C and 25-80bar.

Where coal is the feedstock the ash melts to form a slag. Where oil residues are fired, any metal compounds will leave the reactor in the gas stream and will be recovered in the gas scrubbing system.

Entrained flow gasifiers have been used successfully in the USA (e.g. Texaco Gasifier at Cool Water Project using coal, 1984; Dow Plaquemine commercial power using lignite, 1987). Also, a series of other GCC and IGCC projects are currently being pursued in Europe. Texaco Gasifiers are to be used in three refinery oil residue applications in Italy (Isab, Priolo 507MWe; Api, Falconara 220MWe; and Saras, Cagliari 508MWe). Shell gasifiers are also to be used in the planned gasification projects at Pernis (Shell Refinery) in the Netherlands, where a hydrogen co-product will be produced, and at Porvoo (Neste Oy) in Finland. These systems contain fully proven components linked together by a level of integration which their respective designers believed to be the most appropriate arrangement for the feedstocks being converted. The Netherlands Power Company (Sep) subsidiary Demkolec is using a Shell Entrained Flow Coal Gasifier with a boiler at a 250MWe IGCC demonstration plant at Buggenum in Limburg. At Puertollano, Spain a project using the KruppKoppers Prenflo Gasifier is due to begin commissioning in 1995. This entrained gasifier will be used to gasify mixtures of local high ash coals and high sulphur petroleum coke.

Texaco gasifier

This technology was acquired by General Electric in 2004. In this process, coal is ground and mixed with water to form a slurry. Alternatively refinery oil residues are fed to the gasifier. This is gasified by adding a sub-stoichiometric amount of oxygen via a specially designed burner. Due to the gasification conditions, the gas is rich in hydrogen and carbon monoxide, and sulphur is converted to hydrogen sulphide. Ash leaves the gasification reactor as a molten slag.

Shell gasifier

In this process, coal is ground and injected as a fine dry powder. In contrast to the Texaco process the entrained flow gasifier reactor is fed from the sides and there is a membrane reactor wall. The coal ash content is removed as a slag. A primary heat exchanger (boiler) is part of the Shell gasification system design. The Shell gasifier generally uses a lower oxygen feed rate than the Texaco gasifier and thus the gas produced has a low carbon dioxide level. Shell also has gasifiers designed for oil feedstocks and these are fed from the top and are refractory lined.

Other gasifiers

An operational Dow gasifier at Plaquemine, USA consumes 2100 tons per day of coal/water slurry feed. The E-Gas technology, previously known as the Dow or DESTEC design, is owned by Conoco Phillips and is a two-stage entrained gasifier in which the raw feed is introduced into a second chamber of the reactor to internally cool the products of the first stage. This unit now processes 100% petroleum coke.

The Noell Gasifier technology, commercialised at BASF Seal Sands, UK has also recently been aquired by BASF from Future Energy Limited and has been selected for the possible UK IGCC project at Drym in South Wales. This technology uses a novel design in which moving ash is used to cool the reactor wall, thereby avoiding the need for fixed refractory

Fixed bed gasifiers

In the fixed bed gasifier lump coal of specific size is charged into the top of the reactor through a lock hopper. Fine coal can only be used at levels of up to 40% of the total feed (depending on coal type), the balance will need to be briquetted. Steam and oxygen enter the gasifier near the bottom and flow upwards, counter to the coal flow. The operational pressure of this type of gasifier lies in the range 10-100bar. The bed of coal is not fixed, hence a more correct name for this group of gasifiers is sometimes used - "moving bed gasifiers". The reaction temperature usually lies between 800-1000°C for dry ash plant and 1500-1800°C for the British Gas Lurgi slagger, and therefore the mineral content of the feedstock is released either as ash or as slag. The calorific value of the gas produced by this type of gasifier is higher due to the methane content of the gas produced.

Lurgi fixed bed dry ash gasifier

This is a well established process whereby coal or lignite is gasified by steam/oxygen injection resulting in near total gasification of the feedstock leaving a dry ash to be disposed of from the reactor bottom.

The basic design of fixed bed gasifiers is relatively old. The technology has been successfully used in the UK at Westfield in Scotland, and Coleshill in England. In South Africa the world's largest gasification plant is based on this technology; in North Dakota, U.S.A., about 3.68 million standard m3 per day of synthetic natural gas is produced using dry ash gasifiers. The Lurgi and its higher temperature counterpart, British Gas -Lurgi gasifiers are considered available technology. The British Gas-Lurgi design operates at about 1600°C and as a result produces a molten slag similar to the entrained flow gasifiers.

BG / Lurgi slagging gasifier

This was developed from the original Lurgi gasifiers by British Gas and Lurgi. Early work showed that the efficiency of the dry -ash Lurgi gasifier could be improved significantly by reducing the steam/oxygen ratio and raising reaction temperature so that ash is discharged as liquid slag. British Gas modified one of their Westfield dry-ash units by replacing the rotating grate at the base of the gasifier with a refractory hearth with provision for slag tapping into a quench chamber and slag lock system. Injection of the steam/oxygen supply is achieved via tuyeres in the reactor shell above hearth level.

Fluidised bed gasifiers

Coal, milled to a 1- 5mm size range, is introduced into an upward flow of steam and oxygen adjusted to a flow rate which fluidises the coal. The bed temperature is kept low enough to prevent ash fusion, slagging and clinkering which would disturb the flow patterns within the fluidised bed. Such processes can only achieve high carbon conversions with reactive fuels such as lignite (brown coal). Not all gasifiers of this type are oxygen blown. Some air blown gasifiers have been developed.

High Temperature Winkler

The High Temperature Winkler (HTW) process, applied in one plant in Germany, utilises 730 tonnes per day of brown coal.

This type of gasifier is supposed to be used for an IGCC project (RWE's 300MWe KoBra) in Germany. The syngas goes forward to conventional gas cleaning prior to use, whilst residual bottom and fly ash which still can contain some carbon are burnt in a fluidised bed combustor.

Lurgi Circulating Fluidised Bed (CFB) Gasifier

Coal or other carbonaceous feedstocks are ground to -35mm (e.g. wood) or -5mm (e.g. coal) and fed to a CFB gasifier, along with air or oxygen and steam as required. Operation is slightly above atmospheric pressure. This process is suitable for a wide range of fuels, including coals with ash contents of 50%+ and for low plant capacities.

Air Blown Gasification Cycle (ABGC) (formerly known as the British Coal Topping Cycle)

The Clean Coal Power Generation Group are developing a fluidised bed partial gasifier capable of producing a fuel gas suitable, after removal of particulate matter, for direct use as a fuel for a gas turbine. The process utilises a pressurised gasifier with air fluidisation, fine coal and limestone sorbent being injected separately. It is designed to gasify up to 80% of the coal in the gasifier (i.e. gasification is incomplete) with the remaining char being passed to a fluidised bed combustor (FBC). Dependent on the application, the combustion products from the FBC can be recombined with the gasifier product or used to raise steam etc in separate plant. The process will have a high overall thermal efficiency (~47% with cold gas clean-up rising to over 50% when hot gas clean-up becomes available). The limestone fed to the gasifier partially removes sulphur, the remaining sulphur leaving the gasifier in the gas stream. Due to the added limestone there is a considerable amount of mineral ash available for utilisation or for disposal from the process. Virtually all the NOx produced from the combustion of the low cv gas is fuel NO, Plant sizes for air gasification will be considerably larger than for oxygen gasification in order to accommodate the much larger gas flows. However, air-blown processes preclude the necessity of an air separation unit.

Purification and gas processing

Introduction

Due to the wide range of primary gasification processes available and the effects of variation of feedstocks on primary gas composition, the purification processes applied will be diverse. The general methods are listed but selection of the best available technique is dependent on the use for which the product is intended.

Quenching and cooling

Quenching of the hot reaction gases to temperatures which permit further processing is a primary requirement in some gasification applications and can be achieved either by direct liquid or gas contact or by indirect cooling.

Liquid quenching

This method is used in the Lurgi dry ash and BG / Lurgi processes to reduce the gasifier offtake gases to temperatures permitting further processing. The hot reactor gases are quenched by direct contact with are-circulated aqueous liquor resulting in the condensation of oils and tars and removal of virtually all particulate matter. The liquor produced is then separated into hydrocarbon and aqueous fractions. The hydrocarbon fraction is recycled to the gasifier and part of the aqueous fraction is re-cycled for quenching the hot product gas. A substantial proportion of the ammonia and some acid gases in the primary gas are dissolved in the aqueous liquor. The aqueous liquor has therefore to be treated to recover these gases which can then be incinerated in a Claus unit.

Liquid quenching is also used in the direct quench version of the Texaco gasifier.

Gas re -cycle quenching

In order to protect secondary steam raising plant from excessive temperatures the primary offtake gas from some entrained flow gasifiers (e.g. Shell) is quenched by a cool gas stream, re-cycled from the downstream side of the heat recovery system. This also cools fly slag to below its melting point and permits its removal by cyclones prior to the heat recovery section.

Acid gas and carbon dioxide removal

Acid gases and other gaseous impurities can be removed by a wide variety of processes. The process selected will be dependent on the type of gasifier and feedstock and on the downstream process. For example, where the gas is to be converted to substitute natural gas (SNG) the catalyst used for conversion may be sensitive to poisoning by sulphur compounds and require a feed with a sulphur content of 1ppm or less. Alternatively, where the gas is to be used as a direct fuel, e.g. for a gas turbine, a lower degree of purification may be acceptable both from the process and emission viewpoints. The process selected may therefore vary widely in efficiency from 95% removal of sulphur down to producing a product with less than 1ppm of sulphur. Sulphur removal efficiencies of over 99% are readily attainable. Methods used are normally regenerative liquid phase chemical or physical absorption methods although other processes of a non regenerative nature may be used where the sulphur content of the raw gas is low.

Hot gas clean-up techniques are under investigation and development. Whilst it is premature to assess the achievable levels to which a commercial hot gas clean-up system could operate, indications are that the thermal efficiency of gasification processes using hot gas clean-up techniques would be higher, but at the expense of higher emissions of acid and other gases.

Gas processing

Two of the main processes undertaken are the 'carbon monoxide shift' reaction, which reacts carbon monoxide with water to form carbon dioxide and hydrogen, and methanation, reacting carbon monoxide and hydrogen to produce methane and water.

These reactions can be done as separate stages where the carbon monoxide shift is undertaken before methanation to produce the 3:1 hydrogen to carbon monoxide ratio needed or as a single stage. Processes exist for both routes

1.7.5 Utilities

1.7.5.1 Fuel systems and combustion processes

Most refinery processes include at least one fired heater. Together with steam raising plant, which may include electricity generating facilities and Combined Heat and Power facilities (CHP), these combustion processes are normally fuelled from refinery fuel gas and oil systems. No distinction is made between fired process heaters and boilers in this Note. The capacity of these combustion plants varies widely from less than 10 up to 200 megawatts thermal input (MWth); total installed capacities range from several hundred to 1500MWth or more on the largest refineries.

These plants are an inherent integrated part of the petroleum process and operated primarily for the purpose of the process and thus, their operation is treated as part of the installation. They are major contributors to the release of prescribed substances from refineries, principally oxides of sulphur but also oxides of nitrogen, oxides of carbon and particulate matter.

New units (ie units which came into existence on or after 1 July 1987) with individual furnaces greater than 50MWth or multiple heaters where aggregate thermal input is greater than 50MW, come within the scope of the EC Large Combustion Plant Directive, and must comply with its requirements. However the Directive does not cover direct refinery processes, e.g. FCCU regenerators, coking processes or SRUs.

Process description

A variety of furnaces and burner types are used in refineries, largely determined by the heat release characteristics required by a particular process. Many, but not all, furnaces are dual (oil/gas) fired to allow flexibility in the refinery fuel system. Refinery process heaters are typically rectangular or cylindrical enclosures with multiple up-fired burners of specialised design using mainly low combustion intensity while boilers are generally fairly standard steam producing units of medium or high combustion intensity.

Normally most or all of the fuels used are by -products of refinery processes, both gases and liquids. As a proportion of total crude intake this typically varies from 2-3% for simple refineries to 6-8% for the complete complex refineries.

Refinery Fuel Gas (RFG) is made up of the lighter (typically C1 - C5) overheads from the fractionation stages of many processes and has to be used quickly; thus it supplies the refinery base load energy requirements. Any excess hydrogen is also added to RFG and LPG or natural gas may be used as a balancing fuel. RFGs may be sulphur-free at source (e.g. from catalytic reforming and isomerisation processes) or sulphur-containing (most other gases, e.g. from crude distillation, cracking and all hydrodesulphurising processes). In the latter case gases are normally treated by amine scrubbing before use, as described in Section 0.

Some gases are used locally, i.e. in the process of origin or an adjacent process, however most refineries operate a common RFG main into which most RFG is fed and transferred to the gas users. In a modern refinery the RFG main is carefully "balanced" with respect to supply and demand; necessary flexibility is obtained by operating it between upper and lower pressure limits. The relationship to the refinery flare system is important and RFG will normally include gas received from flare gas recovery. It may also release excess gas to flare if the upper limit pressure is exceeded.

Oil fuels are used to make up the balance of fuel requirements. They are normally pooled and stored before use and are typically the heavier liquid residues from crude distillation, conversion and cracking processes. As such they are liable to contain significant proportions of sulphur, depending mainly on the crude feedstock(s) being processed, ranging from 0.4% for North Sea straight run atmospheric residue up to 6.5% for Middle East cracked residue.

The baseline ratio of gas to oil fuel used on a refinery is a function of a number of factors, important amongst which are the size, degree of complexity, LPG recovery efficiency and extent to which RFG is processed into other products (e.g. olefins) or exported to adjacent chemicals plants (either directly or as energy from common facilities). It varies from 80/20 or 70/30 on a standalone moderately complex refinery to 40/60 on a highly complex site which also services a chemicals complex.

Good design and management of gas and oil fuel systems are important aspects of minimising the environmental impact of a refinery, bearing in mind the highly integrated and interdependent nature of most processes. The normal aim is to match continuously the variable production and consumption of fuels on processes and utilities at the lowest economic and environmental cost.

1.7.5.2 Flares

The production and use of gas from refinery processes is described above. As noted, excess gas cannot be stored, therefore gas surplus to requirements becomes a source of flare gas. A flare system is an essential part of the safe operation of a refinery. It is designed to operate over a wide range of flow conditions ranging from routine/non-emergency flows to start-up/upset/emergency situations on individual processes or site-wide.

Routine or non-emergency sources of flare gas include some process vents, vents from storage and flare system pilot/purge gas. It is possible to install flare facilities to burn gas from non-emergency sources smokelessly, quietly and largely unseen. However this gas can normally be compressed and returned to the fuel gas system or used for power generation, e.g. by CHP.

Upset sources arise from individual pressure reliefs and occasionally during start-up or shut-down of major process units it may be necessary to flare larger quantities of gas. Emergency conditions such as equipment or power failure are likely to create a need to flare very substantial gas quantities, although such emergency flaring is a relatively rare event. Full emergency flare loads normally exceed the range of smokeless operation.

Process description

Process vessels and pipelines incorporate many pressure relief and isolation valves and some vents, most of which are piped to flare headers. These convey gases to the flare(s); a simple refinery may have a single flare whereas a complete complex refinery is likely to have two or three flares. Flares may be dedicated to specific duties (eg HF alkylation or high pressure LPG) or be common to all or most duties. Refineries rely exclusively on high level flares located at the top of tall flare stacks designed mainly on safety criteria, ie acceptable radiant heat at ground level.

The Sector BREF Note gives a full description of flare tip designs and other features and Inspectors should refer to it. Modern flare systems normally incorporate local knock-out/seal pots with gas recovery, continuous multiple pilot burners and have systems (eg steam or air injection) to improve combustion efficiency and enable smokeless flaring to be achieved under non-emergency conditions. Steam supply and injection systems should be designed to minimise operational noise. Sour gas and acid gas can be successfully flared with due care and attention (but see below).

1.7.5.3 Aqueous effluent treatment

The typical sources and types of aqueous effluents may be considered as follows:

- 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 fire-fighting 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 "once-through" systems are used instead of recirculation and steam condensate where not re-used.

Conventional practice is to bring appropriate effluent streams together and to provide common treatment plant(s), which thus become a significant aspect of refinery operation in most cases. Where "once-through" cooling water is used, the flow is likely to be considerably greater in magnitude than all others combined.

Effluent treatment facilities have therefore evolved into a series of devices for dealing with the effluent arisings in an effort to remove and re-cycle as much of the oil as is practicable and to reduce the concentration of polluting substances prior to discharge of the treated aqueous effluent to the environment. Processes used fall into three main categories as follows:

- 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 have been added to improve final effluent quality. The complexity of each refinery affects the composition of the effluent; simpler refineries without cracking processes normally release much less dissolved pollutants such as ammonia and phenols than do the complete complex refineries, which accordingly require a greater extent of treatment. The location, choice and extent of treatment processes are therefore normally site-specific to meet the physical and chemical characteristics of the effluents and also the flowrate and temperature ranges encountered.

Process description

Primary treatment processes

American Petroleum Institute (API) separator

This is a simple gravity separator allowing sufficient residence time for the separation of more buoyant oil particles and settleable solids from the aqueous phase. Inputs to the separators may contain several per cent of oil. They are typically designed to remove all oil globules larger than 150microns and can produce an effluent with an oil content of some 50-100mg/l. 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

These are gravity separators but in a more compact and sophisticated form than the API. A series of compactly arranged inclined plates are provided as surfaces for the oil particles to 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 of some 30-50mg/l is achievable. Versions usually encountered are the parallel plate interceptor (PPI) and the corrugated plate interceptor (CPI); the latter offer highest performance.

Secondary treatment processes

Flocculation/coagulation

In order to aid the main separation process, a prior addition is made of a specific chemical which encourages small oil globules etc, to flocculate and coagulate into larger globules. Refineries normally use a selected organic polyelectrolyte for this; 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 at pressures up to 500kPa and then released via ports into the separator through which the effluent is flowing. A 'champagne effect' results in which air bubbles become attached to oil particles of essentially neutral buoyancy in water, so 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

A series of agitators mix the effluent with air as it flows through a series of chambers so inducing air into it and causing the oil particles to become buoyant as before. The oil is floated off continuously. This type of unit has the advantage that it can be enclosed so minimising hydrocarbon losses to air by vaporisation.

Both techniques have the advantage of adding oxygen to the effluent and removing suspended solids as well as oil particles. Oil levels in effluent can be reduced to 30 mg/l or less, mainly depending on the soluble oil/hydrocarbon content of the effluent.

Filtration techniques

An alternative to flotation methods is the use of media type filtration, typically downflow sand filters, using a number of units in parallel to allow some to be on-line whilst other units are back flushed to collect the deposited solids as a sludge.

Tertiary treatment processes

Biological treatment

Aerobic type biological treatment has been proven to be very effective at breaking down organic compounds and other dissolved pollutants in most refinery effluents and thus reducing the final BOD and COD to acceptable levels. It is probably favoured by the typical moderate year-round warmth of refinery effluents, and successful plants destroy most of the phenols, sulphides, other organics and ammonia in effluents. The process utilises the ability of an acclimatised biomass (mainly bacteria), retained in an appropriate medium, efficiently to digest and oxidise many organic/nitrogen-containing compounds. Available processes include activated sludge units, aerated lagoons, trickle filters, and bio discs. Phenols and sulphides can each be reduced to 1 mg/l or less and reductions of BOD and COD can be up to about 90% and 80% respectively. The biomass needs a sufficient supply of nutrients in the form of nitrogen and phosphorus to work efficiently. Nitrogen is typically available in adequate amount from stripped sour waters (see Section 1.6.2.7) but phosphorus will normally have to be added to feed the bacteria. Air or oxygen is supplied to maintain aerobic conditions. Care is taken that shock loads of materials toxic to the biomass are avoided by diligent management of the effluent-producing processes and pollutant load balancing within the treatment plant.

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

The treated effluent is allowed to travel slowly through sedimentation tanks or ponds, followed if necessary by filtration of the decanted outflow by a suitable device, typically a sand or gravel media filter. The settled solids and those removed from the filter media by back flushing 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) is sometimes used for removal of final traces of oil and suspended solids, with the scavenged effluent being filtered through a media filter.

After clarification of the supernatant final effluent, oil levels of less than 3mg/l can be achieved.

General aspects

Refinery drainage systems, including the effluent treatment facilities, are carefully designed in order to operate safely and efficiently at all times. As well as the hydraulic flow requirements, a particularly important aspect is the avoidance of dangerous concentrations of hydrocarbon vapours which might propagate fire. Thus the systems usually consist of pipes or channels with vented manholes and firetraps at regular intervals along them to maintain invert levels such that the system remains flooded. There may be as many as 40 or 50 manholes between a source of effluent and the first separator. Because of their lower density, any 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 such as caused by severe storms or fire-fighting. Design features include the provision of 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.