

Environmental, Health, and Safety Guidelines for Petroleum Refining

Introduction

The Environmental, Health, and Safety (EHS) Guidelines are technical reference documents with general and industry-specific examples of Good International Industry Practice (GIIP)¹. When one or more members of the World Bank Group are involved in a project, these EHS Guidelines are applied as required by their respective policies and standards. These industry sector EHS guidelines are designed to be used together with the **General EHS Guidelines** document, which provides guidance to users on common EHS issues potentially applicable to all industry sectors. For complex projects, use of multiple industry-sector guidelines may be necessary. A complete list of industry-sector guidelines can be found at: www.ifc.org/ifcext/enviro.nsf/Content/EnvironmentalGuidelines

The EHS Guidelines contain the performance levels and measures that are generally considered to be achievable in new facilities by existing technology at reasonable costs. Application of the EHS Guidelines to existing facilities may involve the establishment of site-specific targets, with an appropriate timetable for achieving them. The applicability of the EHS Guidelines should be tailored to the hazards and risks established for each project on the basis of the results of an environmental assessment in which site-specific variables, such as host country context, assimilative capacity of the environment, and other project factors, are taken into account.

¹ Defined as the exercise of professional skill, diligence, prudence and foresight that would be reasonably expected from skilled and experienced professionals engaged in the same type of undertaking under the same or similar circumstances globally. The circumstances that skilled and experienced professionals may find when evaluating the range of pollution prevention and control techniques available to a project may include, but are not limited to, varying levels of environmental degradation and environmental assimilative capacity as well as varying levels of financial and technical feasibility.

The applicability of specific technical recommendations should be based on the professional opinion of qualified and experienced persons. When host country regulations differ from the levels and measures presented in the EHS Guidelines, projects are expected to achieve whichever is more stringent. If less stringent levels or measures than those provided in these EHS Guidelines are appropriate, in view of specific project circumstances, a full and detailed justification for any proposed alternatives is needed as part of the site-specific environmental assessment. This justification should demonstrate that the choice for any alternate performance levels is protective of human health and the environment.

Applicability

The EHS Guidelines for Petroleum Refining cover processing operations from crude oil to finished liquid products, including liquefied petroleum gas (LPG), Mo-Gas (motor gasoline), kerosene, diesel oil, heating oil, fuel oil, bitumen, asphalt, sulfur, and intermediate products (e.g. propane / propylene mixtures, virgin naphtha, middle distillate and vacuum distillate) for the petrochemical industry. Annex A contains a description of industry sector activities. Further information on EHS issues related to storage tank farms is provided in the EHS Guidelines for Crude Oil and Petroleum Product Terminals. This document is organized according to the following sections:

Section 1.0 — Industry-Specific Impacts and Management
Section 2.0 — Performance Indicators and Monitoring
Section 3.0 — References and Additional Sources
Annex A — General Description of Industry Activities

1.0 Industry-Specific Impacts and Management

The following section provides a summary of EHS issues associated with petroleum refining which occur during the operational phase, along with recommendations for their management. Recommendations for the management of EHS issues common to most large industrial facilities during the construction and decommissioning phases are provided in the **General EHS Guidelines**.

1.1 Environmental

Potential environmental issues associated with petroleum refining include the following:

- Air emissions
- Wastewater
- Hazardous materials
- Wastes
- Noise

Air Emissions

Exhaust Gases

Exhaust gas and flue gas emissions (carbon dioxide (CO₂), nitrogen oxides (NO_x) and carbon monoxide (CO)) in the petroleum refining sector result from the combustion of gas and fuel oil or diesel in turbines, boilers, compressors and other engines for power and heat generation. Flue gas is also generated in waste heat boilers associated with some process units during continuous catalyst regeneration or fluid petroleum coke combustion. Flue gas is emitted from the stack to the atmosphere in the Bitumen Blowing Unit, from the catalyst regenerator in the Fluid Catalytic Cracking Unit (FCCU) and the Residue Catalytic Cracking Unit (RCCU), and in the sulfur plant, possibly containing small amounts of sulfur oxides. Low-NO_x burners should be used to reduce nitrogen oxide emissions.

Air quality impacts should be estimated by the use of baseline air quality assessments and atmospheric dispersion models to establish potential ground level ambient air concentrations during facility design and operations planning as described in the **General EHS Guidelines**.

Guidance for the management of small combustion source emissions with a capacity of up to 50 megawatt thermal (MWth), including air emission standards for exhaust emissions, is provided in the **General EHS Guidelines**. For combustion source emissions with a capacity of greater than 50 MWth, refer to the **EHS Guidelines for Thermal Power**.

Venting and Flaring

Venting and flaring are important operational and safety measures used in petroleum refining facilities to ensure that vapors gases are safely disposed of. Petroleum hydrocarbons are emitted from emergency process vents and safety valves discharges. These are collected into the blow-down network to be flared.

Excess gas should not be vented, but instead sent to an efficient flare gas system for disposal. Emergency venting may be acceptable under specific conditions where flaring of the gas stream is not possible, on the basis of an accurate risk analysis and integrity of the system needs to be protected. Justification for not using a gas flaring system should be fully documented before an emergency gas venting facility is considered.

Before flaring is adopted, feasible alternatives for the use of the gas should be evaluated and integrated into production design to the maximum extent possible. Flaring volumes for new facilities should be estimated during the initial commissioning period so that fixed volume flaring targets can be developed. The volumes of gas flared for all flaring events should be recorded and reported. Continuous improvement of flaring

through implementation of best practices and new technologies should be demonstrated.

The following pollution prevention and control measures should be considered for gas flaring:

- Implementation of source gas reduction measures to the maximum extent possible;
- Use of efficient flare tips, and optimization of the size and number of burning nozzles;
- Maximizing flare combustion efficiency by controlling and optimizing flare fuel / air / steam flow rates to ensure the correct ratio of assist stream to flare stream;
- Minimizing flaring from purges and pilots, without compromising safety, through measures including installation of purge gas reduction devices, flare gas recovery units, inert purge gas, soft seat valve technology where appropriate, and installation of conservation pilots;
- Minimizing risk of pilot blow-out by ensuring sufficient exit velocity and providing wind guards;
- Use of a reliable pilot ignition system;
- Installation of high integrity instrument pressure protection systems, where appropriate, to reduce over pressure events and avoid or reduce flaring situations;
- Installation of knock-out drums to prevent condensate emissions, where appropriate;
- Minimizing liquid carry-over and entrainment in the gas flare stream with a suitable liquid separation system;
- Minimizing flame lift off and / or flame lick;
- Operating flare to control odor and visible smoke emissions (no visible black smoke);
- Locating flare at a safe distance from local communities and the workforce including workforce accommodation units;
- Implementation of burner maintenance and replacement programs to ensure continuous maximum flare efficiency;

- Metering flare gas.

To minimize flaring events as a result of equipment breakdowns and plant upsets, plant reliability should be high (>95 percent), and provision should be made for equipment sparing and plant turn down protocols.

Fugitive Emissions

Fugitive emissions in petroleum refining facilities are associated with vents, leaking tubing, valves, connections, flanges, packings, open-ended lines, floating roof storage tanks and pump seals, gas conveyance systems, compressor seals, pressure relief valves, tanks or open pits / containments, and loading and unloading operations of hydrocarbons. Depending on the refinery process scheme, fugitive emissions may include:

- Hydrogen;
- Methane;
- Volatile organic compounds (VOCs), (e.g. ethane, ethylene, propane, propylene, butanes, butylenes, pentanes, pentenes, C₆-C₉ alkylate, benzene, toluene, xylenes, phenol, and C₉ aromatics);
- Polycyclic aromatic hydrocarbons (PAHs) and other semivolatile organic compounds;
- Inorganic gases, including hydrofluoric acid from hydrogen fluoride alkylation, hydrogen sulfide, ammonia, carbon dioxide, carbon monoxide, sulfur dioxide and sulfur trioxide from sulfuric acid regeneration in the sulfuric acid alkylation process, NO_x, methyl tert-butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), t-amylmethyl ether (TAME), methanol, and ethanol.

The main sources of concern include VOC emissions from cone roof storage tanks during loading and due to out-breathing; fugitive emissions of hydrocarbons through the floating roof seals of floating roof storage tanks; fugitive emissions from flanges and/or valves and machinery seals; VOC emissions

from blending tanks, valves, pumps and mixing operations; and VOC emissions from oily sewage and wastewater treatment systems. Nitrogen from bitumen storage tanks may also be emitted, possibly containing hydrocarbons and sulfur compounds in the form of aerosols. Other potential fugitive emission sources include the Vapor Recovery Unit vents and gas emission from caustic oxidation.

Recommendations to prevent and control fugitive emissions include the following:

- Based on review of Process and Instrumentation Diagrams (P&IDs), identify streams and equipment (e.g. from pipes, valves, seals, tanks and other infrastructure components) likely to lead to fugitive VOC emissions and prioritize their monitoring with vapor detection equipment followed by maintenance or replacement of components as needed;
- The selection of appropriate valves, flanges, fittings, seals, and packings should be based on their capacity to reduce gas leaks and fugitive emissions;
- Hydrocarbon vapors should be either contained or routed back to the process system, where the pressure level allows;
- Use of vent gas scrubbers should be considered to remove oil and other oxidation products from overhead vapors in specific units (e.g. bitumen production);
- Incineration of gas should be conducted at high temperature (approximately 800 °C) to ensure complete destruction of minor components (e.g. H₂S, aldehydes, organic acids and phenolic components) and minimize emissions and odor impacts;
- Emissions from hydrofluoric acid (HF) alkylation plant vents should be collected and neutralized for HF removal in a scrubber before being sent to flare;

- Naphtha, gasoline, methanol / ethanol, and MTBE / ETBE / TAME loading / unloading stations should be provided with vapor recovery units.

Additional guidelines for the prevention and control of fugitive emissions from storage tanks are provided in the **EHS Guidelines for Crude Oil and Petroleum Product Terminals**.

Sulfur Oxides

Sulfur oxides (SO_x) and hydrogen sulfide may be emitted from boilers, heaters, and other process equipment, based on the sulfur content of the processed crude oil. Sulfur dioxide and sulfur trioxide may be emitted from sulfuric acid regeneration in the sulfuric acid alkylation process. Sulfur dioxide in refinery waste gases may have pre-abatement concentration levels of 1500 -7500 milligrams per cubic meter (mg/m³).²

Recommended pollution prevention and minimization measures include the following:

- Minimize SO_x emissions through desulfurization of fuels, to the extent feasible, or by directing the use of high-sulfur fuels to units equipped with SO_x emission controls;
- Recover sulfur from tail gases using high efficiency sulfur recovery units (e.g. Claus units);³
- Install mist precipitators (e.g. electrostatic precipitators or brink demisters) to remove sulfuric acid mist;
- Install scrubbers with caustic soda solution to treat flue gases from the alkylation unit absorption towers.

Particulate Matter

Particulate emissions from refinery units are associated with flue gas from furnaces; catalyst fines emitted from fluidized catalytic cracking regeneration units and other catalyst based processes;

² EIPPCB BREF (2003)

³ A sulfur recovery system with at least 97 percent but preferably over 99 percent sulfur recovery should be used when the hydrogen sulfide concentration in tail gases is significant.

the handling of coke; and fines and ash generated during incineration of sludges. Particulates may contain metals (e.g. vanadium, nickels). Measures to control particulate may also contribute to control of metal emissions from petroleum refining.⁴

Recommended pollution prevention and minimization measures include the following:

- Install cyclones, electrostatic precipitators, bag filters, and/or wet scrubbers to reduce emissions of particulates from point sources. A combination of these techniques may achieve >99 percent abatement of particulate matter;
- Implement particulate emission reduction techniques during coke handling, including:
 - Store coke in bulk under enclosed shelters
 - Keep coke constantly wet
 - Cut coke in a crusher and convey it to an intermediate storage silo (hydrobins)
 - Spray the coke with a fine layer of oil, to stick the dust fines to the coke
 - Use covered and conveyor belts with extraction systems to maintain negative pressure
 - Use aspiration systems to extract and collect coke dust
 - Pneumatically convey the fines collected from the cyclones into a silo fitted with exit air filters, and recycle the collected fines to storage.

Greenhouse Gases (GHGs)

Carbon dioxide (CO₂) may be produced in significant amounts during petroleum refining from combustion processes (e.g. electric power production), flares, and hydrogen plants. Carbon dioxide and other gases (e.g. nitrogen oxides and carbon

monoxide) may be discharged to atmosphere during in-situ catalyst regeneration of noble metals.

Operators should aim to maximize energy efficiency and design facilities (e.g. opportunities for efficiency improvements in utilities, fired heaters, process optimization, heat exchangers, motor and motor applications) to minimize energy use. The overall objective should be to reduce air emissions and evaluate cost-effective options for reducing emissions that are technically feasible.⁵ Additional recommendations for the management of GHGs, in addition to energy efficiency and conservation, are addressed in the **General EHS Guidelines**.

Wastewater

Industrial Process Wastewater

The largest volume effluents in petroleum refining include "sour" process water and non-oily/non-sour but highly alkaline process water. Sour water is generated from desalting, topping, vacuum distillation, pretreating, light and middle distillate hydrodesulphurization, hydrocracking, catalytic cracking, coking, visbreaking / thermal cracking. Sour water may be contaminated with hydrocarbons, hydrogen sulfide, ammonia, organic sulfur compounds, organic acids, and phenol. Process water is treated in the sour water stripper unit (SWS) to remove hydrocarbons, hydrogen sulfide, ammonia and other compounds, before recycling for internal process uses, or final treatment and disposal through an onsite wastewater treatment unit. Non-oily / non-sour but highly alkaline process water has the potential to cause Waste Water Treatment Plant upsets. Boiler blowdown and demineralization plant reject streams in particular, if incorrectly neutralized, have the potential to extract phenolics from the oil phase into the water phase, as well as cause emulsions in the WWTP. Liquid effluent may also result from

⁴ EIIPCB BREF (2003)

⁵ Detailed information on energy efficiency opportunities for petroleum refineries is presented in Energy Efficiency Improvement and Cost Saving Opportunities for Petroleum Refineries, Ernest Orlando Lawrence Berkeley National Laboratory, University of California, 2005, available at: <http://repositories.cdlib.org/cgi/viewcontent.cgi?article=3856&context=lbln>

accidental releases or leaks of small quantities of products from process equipment, machinery and storage areas/tanks.

Recommended process wastewater management practices include:

- Prevention and control of accidental releases of liquids through regular inspections and maintenance of storages and conveyance systems, including stuffing boxes on pumps and valves and other potential leakage points, as well as the implementation of spill response plans;
- Provision of sufficient process fluids let-down capacity to maximize recovery into the process and avoid massive discharge of process liquids into the oily water drainage system;
- Design and construction of wastewater and hazardous materials storage containment basins with impervious surfaces to prevent infiltration of contaminated water into soil and groundwater;
- Segregation of process water from stormwater and segregation of wastewater and hazardous materials containment basins;
- Implementation of good housekeeping practices, including conducting product transfer activities over paved areas and prompt collection of small spills.

Specific provisions to be considered for the management of individual wastewater streams include the following:

- Direct spent caustic soda from sweetening units and chemical treating routed to the wastewater treatment system following caustic oxidation;
- Direct spent caustic liquor from the caustic oxidation (containing soluble thiosulfates, sulfites and sulfates) to the wastewater treatment system;
- Install a closed process drain system to collect and recover leakages and spills of MTBE, ETBE, and TAME. These

substances are not conducive to biological treatment, and should be prevented from entering and adversely affecting the wastewater treatment system;

- If present at the facility, acidic and caustic effluents from the demineralized water preparation should be neutralized prior to discharge into the wastewater treatment system;
- Cool blowdown from the steam generation systems prior to discharge. This effluent, as well as blowdown from cooling water towers, may contain additives (e.g. biocides) and may require treatment in the wastewater treatment plant prior to discharge;
- Hydrocarbons contaminated water from scheduled cleaning activities during facility turn-around (cleaning activities typically are performed annually and may last several few weeks) and hydrocarbon-containing effluents from process leaks should be treated in the wastewater treatment plant.

Process Wastewater Treatment

Techniques for treating industrial process wastewater in this sector include source segregation and pretreatment of concentrated wastewater streams. Typical wastewater treatment steps include: grease traps, skimmers, dissolved air floatation or oil water separators for separation of oils and floatable solids; filtration for separation of filterable solids; flow and load equalization; sedimentation for suspended solids reduction using clarifiers; biological treatment, typically aerobic treatment, for reduction of soluble organic matter (BOD); chemical or biological nutrient removal for reduction in nitrogen and phosphorus; chlorination of effluent when disinfection is required; dewatering and disposal of residuals in designated hazardous waste landfills. Additional engineering controls may be required for (i) containment and treatment of volatile organics stripped from various unit operations in the wastewater treatment system, (ii) advanced metals removal using membrane filtration or other physical/chemical treatment technologies, (iii)

removal of recalcitrant organics and non biodegradable COD using activated carbon or advanced chemical oxidation, (iii) reduction in effluent toxicity using appropriate technology (such as reverse osmosis, ion exchange, activated carbon, etc.), and (iv) containment and neutralization of nuisance odors.

Management of industrial wastewater and examples of treatment approaches are discussed in the **General EHS Guidelines**. Through use of these technologies and good practice techniques for wastewater management, facilities should meet the Guideline Values for wastewater discharge as indicated in the relevant table of Section 2 of this industry sector document.

Other Wastewater Streams & Water Consumption

Guidance on the management of non-contaminated wastewater from utility operations, non-contaminated stormwater, and sanitary sewage is provided in the **General EHS Guidelines**. Contaminated streams should be routed to the treatment system for industrial process wastewater. Recommendations to reduce water consumption, especially where it may be a limited natural resource, are provided in the **General EHS Guidelines**.

Hydrostatic Testing Water: Hydrostatic testing (hydro-test) of equipment and pipelines involves pressure testing with water (generally filtered raw-water), to verify system integrity and to detect possible leaks. Chemical additives (e.g. a corrosion inhibitor, an oxygen scavenger, and a dye) are often added to the water to prevent internal corrosion. In managing hydrotest waters, the following pollution prevention and control measures should be implemented:

- Using the same water for multiple tests;
- Reducing the need for corrosion inhibitors and other chemicals by minimizing the time that test water remains in the equipment or pipeline;

- If chemical use is necessary, selection of effective chemicals with the lowest toxicity, biodegradability, bioavailability, and bioaccumulation potential.

If discharge of hydrotest waters to the sea or to surface water is the only feasible alternative for disposal, a hydrotest water disposal plan should be prepared that considers points of discharge, rate of discharge, chemical use and dispersion, environmental risk, and required monitoring. Hydrotest water disposal into shallow coastal waters should be avoided.

Hazardous Materials

Petroleum refining facilities manufacture, use, and store significant amounts of hazardous materials, including raw materials, intermediate / final products and by-products. Recommended practices for hazardous material management, including handling, storage, and transport, are presented in the **EHS Guidelines for Crude Oil and Petroleum Product Terminals** and in the **General EHS Guidelines**.

Wastes

Hazardous Wastes: Spent Catalysts

Spent catalysts result from several process units in petroleum refining including the pretreating and catalytic reformer; light and middle distillate hydrodesulphurization; the hydrocracker; fluid catalytic cracking (FCCU); residue catalytic cracking (RCCU); MTBE/ETBE and TAME production; butanes isomerization; the dienes hydrogenation and butylenes hydroisomerization unit; sulfuric acid regeneration; selective catalytic hydrodesulphurization; and the sulfur and hydrogen plants. Spent catalysts may contain molybdenum, nickel, cobalt, platinum, palladium, vanadium iron, copper and silica and/or alumina, as carriers.

Recommended management strategies for catalysts include the following:

- Use long life catalysts and regeneration to extend the catalyst life cycle;
- Use appropriate on-site storage and handling methods, (e.g., submerging pyrophoric spent catalysts in water during temporary storage and transport until they can reach the final point of treatment to avoid uncontrolled exothermic reactions);
- Return spent catalysts to the manufacturer for regeneration or recovery, or transport to other off-site management companies for handling, heavy or precious metals recovery / recycling, and disposal in accordance with industrial waste management recommendations included in **General EHS Guidelines**.
- Send oily sludges from crude oil storage tanks and the desalter to the delayed coking drum, where applicable, to recover the hydrocarbons;
- Ensure excessive cracking is not conducted in the visbreaking unit to prevent production of an unstable fuel oil, resulting in increased sludge and sediment formation during storage;
- Maximize recovery of oil from oily wastewaters and sludges. Minimize losses of oil to the effluent system. Oil can be recovered from slops using separation techniques (e.g. gravity separators and centrifuges);
- Sludge treatment may include land application (bioremediation), or solvent extraction followed by combustion of the residue and / or use in asphalt, where feasible. In some cases, the residue may require stabilization prior to disposal to reduce the leachability of toxic metals.

Other Hazardous Wastes

In addition to spent catalysts, industry hazardous waste may include solvents, filters, mineral spirits, used sweetening, spent amines for CO₂, hydrogen sulfide (H₂S) and carbonyl sulfide (COS) removal, activated carbon filters and oily sludge from oil / water separators, tank bottoms, and spent or used operational and maintenance fluids (e.g. oils and test liquids). Other hazardous wastes, including contaminated sludges, sludge from jet water pump circuit purification, exhausted molecular sieves, and exhausted alumina from hydrofluoric (HF) alkylation, may be generated from crude oil storage tanks, desalting and topping, coking, propane, propylene, butanes streams dryers, and butanes isomerization.

Process wastes should be tested and classified as hazardous or non-hazardous based on local regulatory requirements or internationally accepted approaches. Detailed guidance on the storage, handling, treatment, and disposal of hazardous and non-hazardous wastes is provided in the **General EHS Guidelines**.

Recommended industry-specific management strategies for hazardous waste include the following:

Non-hazardous Wastes

Hydrofluoric acid alkylation produces neutralization sludges which may contain calcium fluoride, calcium hydroxide, calcium carbonate, magnesium fluoride, magnesium hydroxide and magnesium carbonate. After drying and compression, they may be marketed for steel mills use or landfilled. Detailed guidance on the storage, handling, treatment, and disposal of non-hazardous wastes is provided in the **General EHS Guidelines**.

Noise

The principal sources of noise in petroleum refining facilities include large rotating machines, such as compressors and turbines, pumps, electric motors, air coolers (if any), and heaters. During emergency depressurization, high noise levels can be generated due to high pressure gases to flare and/or steam release into the atmosphere. General recommendations for noise management are provided in the **General EHS Guidelines**.

1.2 Occupational Health and Safety

The occupational health and safety issues that may occur during the construction and decommissioning of petroleum refining facilities are similar to those of other industrial facilities, and their management is discussed in the **General EHS Guidelines**.

Facility-specific occupational health and safety issues should be identified based on job safety analysis or comprehensive hazard or risk assessment, using established methodologies such as a hazard identification study [HAZID], hazard and operability study [HAZOP], or a quantitative risk assessment [QRA]. As a general approach, health and safety management planning should include the adoption of a systematic and structured approach for prevention and control of physical, chemical, biological, and radiological health and safety hazards described in the **General EHS Guidelines**.

The most significant occupational health and safety hazards occur during the operational phase of a petroleum refining facility and primarily include:

- Process Safety
- Oxygen-deficient atmosphere
- Chemical hazards
- Fire and explosions

Process Safety

Process safety programs should be implemented, due to industry-specific characteristics, including complex chemical reactions, use of hazardous materials (e.g. toxic, reactive, flammable or explosive compounds), and multi-step reactions.

Process safety management includes the following actions:

- Physical hazard testing of materials and reactions;

- Hazard analysis studies to review the process chemistry and engineering practices, including thermodynamics and kinetics;
- Examination of preventive maintenance and mechanical integrity of the process equipment and utilities;
- Worker training; and
- Development of operating instructions and emergency response procedures.

Oxygen-Deficient Atmosphere

The potential release and accumulation of nitrogen gas into work areas may result in the creation of asphyxiating conditions due to the displacement of oxygen. Prevention and control measures to reduce risks of asphyxiant gas release include:

- Design and placement of nitrogen venting systems according to industry standards;
- Installation of an automatic Emergency Shutdown System that can detect and warn of the uncontrolled release of nitrogen (including the presence of oxygen deficient atmospheres in working areas⁶), initiate forced ventilation, and minimize the duration of releases;
- Implementation of confined space entry procedures as described in the **General EHS Guidelines** with consideration of facility-specific hazards.

Chemical Hazards

Releases of hydrofluoric acid, carbon monoxide, methanol and hydrogen sulfide may present occupational exposure hazards. Hydrogen sulfide leakage may occur from amine regeneration in amine treatment units and sulfur recovery units. Carbon monoxide leakage may occur from Fluid and Residue Catalytic Cracking Units and from the syngas production section of the

⁶ Working areas with the potential for oxygen deficient atmospheres should be equipped with area monitoring systems capable of detecting such conditions. Workers also should be equipped with personal monitoring systems. Both types of monitoring systems should be equipped with a warning alarm set at 19.5 percent concentration of O₂ in air.

Hydrogen Plant. Carbon monoxide / air mixtures are explosive and spontaneous / explosive re-ignition may occur. Hydrogen sulfide poses an immediate fire hazard when mixed with air.

Workers may be exposed to potential inhalation hazards (e.g. hydrogen sulfide, carbon monoxide, VOCs, polycyclic aromatic hydrocarbons (PAHs) during routine plant operations. Dermal hazards may include contact with acids, steam, and hot surfaces. Chemical hazards should be managed based on the results of a job safety analysis and industrial hygiene survey and according to the occupational health and safety guidance provided in the **General EHS Guidelines**. Protection measures include worker training, work permit systems, use of personal protective equipment (PPE), and toxic gas detection systems with alarms.⁷

Hydrofluoric Acid

Workers may be exposed to hydrofluoric acid (HF) in the HF alkylation unit. Occupational safety measures include the following:⁸

- Reducing HF volatility by adding suitable vapor pressure suppression additives;
- Minimizing HF hold-up;
- Designing plant lay-out to limit the extent of the plant area exposed to potential HF hazards, and to facilitate escape routes for workers;
- Clearly identifying hazardous HF areas, and indicating where PPE should be adopted;
- Implementing a worker decontamination procedure in a dedicated area;

⁷ A detailed description of health and safety issues and prevention/control strategies associated with petroleum refining, including chemical and fire/explosion hazards, is available in Occupational Safety and Health Association (OSHA) Technical Manual, Section IV Safety Hazards, Chapter 2. (1999) Petroleum Refining Process, available at http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html

⁸ Recommendations for handling of hydrofluoric acid are available in API Recommended Practice RP 751. Safe Operation of Hydrofluoric Acid Alkylation Units (1999).

- Implementing a safety distance buffer between the HF Alkylation Unit, other process units and the refinery boundary;
- Use of scrubbing systems to neutralizing and remove HF prior to flaring;
- Use of a HF neutralization basin for effluents before they are discharged into the refinery oily sewage system;
- Use of a dedicated tank to collect alkylate product and undertake routine pH measurements before dispatching to gasoline pool;
- Treating butane and propane products in alumina defluorinators to destroy organic fluorides, followed by alkali to remove any remaining HF ;
- Transport of HF to and from the plant should be handled according to guidance for the transport of dangerous goods as described in the **General EHS Guidelines**.

Fire and Explosions

Fire and explosion hazards generated by process operations include the accidental release of syngas (containing carbon monoxide and hydrogen), oxygen, methanol, and refinery gases. Refinery gas releases may cause 'jet fires', if ignited in the release section, or give rise to a vapor cloud explosion (VCE), fireball or flash fire, depending on the quantity of flammable material involved and the degree of confinement of the cloud. Methane, hydrogen, carbon monoxide, and hydrogen sulfide may ignite even in the absence of ignition sources, if their temperature is higher than their auto ignition temperatures of 580°C, 500°C, 609°C, and 260°C, respectively. Flammable liquid spills present in petroleum refining facilities may cause pool fires. Explosive hazards may also be associated with accumulation of vapors in storage tanks (e.g. sulfuric acid and bitumen).

Recommended measures to prevent and control fire and explosion risks from process operations include the following:⁹

- Designing, constructing, and operating petroleum refineries according to international standards¹⁰ for the prevention and control of fire and explosion hazards, including provisions for segregation of process, storage, utility, and safe areas. Safety distances can be derived from specific safety analyses for the facility, and through application of internationally recognized fire safety standards;¹¹
- Providing early release detection, such as pressure monitoring of gas and liquid conveyance systems, in addition to smoke and heat detection for fires;
- Evaluation of potential for vapor accumulation in storage tanks and implementation of prevention and control techniques (e.g. nitrogen blanketing for sulfuric acid and bitumen storage);
- Avoiding potential sources of ignition (e.g. by configuring the layout of piping to avoid spills over high temperature piping, equipment, and / or rotating machines);
- Providing passive fire protection measures within the modeled fire zone that are capable of withstanding the fire temperature for a time sufficient to allow the operator to implement the appropriate fire mitigation strategy;
- Limiting the areas that may be potentially affected by accidental releases by:
 - Defining fire zones and equipping them with a drainage system to collect and convey accidental releases of flammable liquids to a safe containment

area, including secondary containment of storage tanks

- Installing fire / blast partition walls in areas where appropriate separation distances cannot be achieved;
- Designing the oily sewage system to avoid propagation of fire.

Further recommendations on the management of fire and explosion hazards relating to crude oil storage are addressed in the **EHS Guidelines for Crude Oil and Petroleum Product Terminals**.

1.3 Community Health and Safety

Community health and safety impacts during the construction and decommissioning of petroleum refining facilities are common to those of most other industrial facilities and are discussed in the **General EHS Guidelines**.

The most significant community health and safety hazards associated with petroleum refining facilities occur during the operational phase including the threat from major accidents related to fires and explosions at the facility and potential accidental releases of raw materials or finished products during transportation outside the processing facility. Guidance for the management of these issues is presented below and in the **General EHS Guidelines**.

Additional relevant guidance applicable to the transport by sea and rail as well as shore-based facilities can be found in the EHS Guidelines for Shipping; Railways; Ports and Harbors; and Crude Oil and Petroleum Products Terminals.

⁹ Further recommendations for fire and explosion hazards are available in API Recommended Practice RP 2001. Fire Protection in Refineries (2005).

¹⁰ An example of good practice includes the US National Fire Protection Association (NFPA) Code 30: Flammable and Combustible Liquids. Further guidance to minimize exposure to static electricity and lightning is available in API Recommended Practice: Protection Against Ignitions Arising out of Static, Lightning, and Stray Currents (2003).

¹¹ An example of further information on safe spacing is the US National Fire Protection Association (NFPA) Code 30.

Major Hazards¹²

The most significant safety hazards are related to the handling and storage of liquid and gaseous substances. Impacts may include significant exposures to workers and, potentially, to surrounding communities, depending on the quantities and types of accidentally released chemicals and the conditions for reactive or catastrophic events, such as fire and explosion.¹³

Major hazards should be prevented through the implementation of a Process Safety Management Program that includes all of the minimum elements outlined in the respective section of the **General EHS Guidelines** including:

- Facility wide risk analysis, including a detailed consequence analysis for events with a likelihood above 10⁻⁶/year (e.g. HAZOP, HAZID, or QRA);
- Employee training on operational hazards;
- Procedures for management of change in operations, process hazard analysis, maintenance of mechanical integrity, pre-start review, hot work permits, and other essential aspects of process safety included in the General EHS Guideline;
- Safe Transportation Management System as noted in the **General EHS Guidelines** if the project includes a transportation component for raw or processed materials;
- Procedures for handling and storage of hazardous materials;
- Emergency planning, which should include, at a minimum, the preparation and implementation of an Emergency Management Plan, prepared with the participation of local authorities and potentially affected communities.

¹² A detailed description of health and safety issues and prevention / control strategies associated with petroleum refining, is available in Occupational Safety and Health Association (OSHA) Technical Manual, Section IV Safety Hazards, Chapter 2 "Petroleum Refining Process", 1999, available at http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html

¹³ Further recommendations for fire and explosion hazards are available in API Recommended Practice RP 2001 "Fire Protection in Refineries", 2005.

2.0 Performance Indicators and Monitoring

2.1 Environment

Emissions and Effluent Guidelines

Tables 1 and 2 present emission and effluent guidelines for this sector. Guideline values for process emissions and effluents in this sector are indicative of good international industry practice as reflected in relevant standards of countries with recognized regulatory frameworks. The guidelines are assumed to be achievable under normal operating conditions in appropriately designed and operated facilities through the application of pollution prevention and control techniques discussed in the preceding sections of this document.

Combustion source emissions guidelines associated with steam- and power-generation activities from sources with a capacity equal to or lower than 50 MWth are addressed in the **General EHS Guidelines** with larger power source emissions addressed in the **Thermal Power EHS Guidelines**. Guidance on ambient considerations based on the total load of emissions is provided in the **General EHS Guidelines**.

Effluent guidelines are applicable for direct discharges of treated effluents to surface waters for general use. Site-specific discharge levels may be established based on the availability and conditions in use of publicly operated sewage collection and treatment systems or, if discharged directly to surface waters, on the receiving water use classification as described in the **General EHS Guidelines**.

Table 1. Air Emissions Levels for Petroleum Refining Facilities^a

Pollutant	Units	Guideline Value
NO _x	mg/Nm ³	450
SO _x	mg/Nm ³	150 for sulfur recovery units; 500 for other units
Particulate Matter	mg/Nm ³	50
Vanadium	mg/Nm ³	5
Nickel	mg/Nm ³	1
H ₂ S	mg/Nm ³	10

a. Dry gas at 3 percent O₂.

Environmental Monitoring

Environmental monitoring programs for this sector should be implemented to address all activities that have been identified to have potentially significant impacts on the environment, during normal operations and upset conditions. Environmental monitoring activities should be based on direct or indirect indicators of emissions, effluents, and resource use applicable to the particular project. Monitoring frequency should be sufficient to provide representative data for the parameter being monitored. Monitoring should be conducted by trained individuals following monitoring and record-keeping procedures and using properly calibrated and maintained equipment. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Additional guidance on applicable sampling and analytical methods for emissions and effluents is provided in the **General EHS Guidelines**.

Resource Use, Energy Consumption, Emission and Waste Generation

Tables 3 and 4 provide examples of resource consumption, and emission / waste quantities generated per million tons of processed crude oil. Industry benchmark values are provided for

comparative purposes only and individual projects should target continual improvement in these areas.

Table 2. Effluent Levels for Petroleum Refining Facilities^a

Pollutant	Units	Guideline Value
pH	S.U.	6-9
BOD ₅	mg/L	30
COD	mg/L	150
TSS	mg/L	30
Oil and Grease	mg/L	10
Chromium (total)	mg/L	0.5
Chromium (hexavalent)	mg/L	0.05
Copper	mg/L	0.5
Iron	mg/L	3
Cyanide Total	mg/L	1
Free		0.1
Lead	mg/L	0.1
Nickel	mg/L	0.5
Mercury	mg/L	0.02
Vanadium	mg/L	1
Phenol	mg/L	0.2
Benzene	mg/L	0.05
Benzo(a)pyrene	mg/L	0.05
Sulfides	mg/L	1
Total Nitrogen	mg/L	10 ^b
Total Phosphorus	mg/L	2
Temperature increase	°C	<3 ^c

Notes:

- Assumes an integrated petroleum refining facility
- The effluent concentration of nitrogen (total) may be up to 40 mg/l in processes that include hydrogenation.
- At the edge of a scientifically established mixing zone which takes into account ambient water quality, receiving water use, potential receptors and assimilative capacity.

Table 3. Resource and Energy Consumption¹

Parameter	Unit	Industry Benchmark
Land Use ⁽¹⁾	hectares	200-500
Total Energy ⁽¹⁾	MJ per Metric Ton of processed crude oil	2,100 – 2,900
Electric Power ⁽¹⁾⁽²⁾	KWh per Metric Ton of processed crude oil	25 - 48
Fresh Make-up Water	m ³ per Metric Ton of processed crude oil	0.07 – 0.14

Notes:
1. Based in part on EC BREF for Refineries
2. Greenfield facilities

Table 4. Emission and Waste Generation¹

Parameter	Unit	Industry Benchmark
Waste water		0.1 - 5
Emissions		
Carbon dioxide	Tons / million tons of processed crude oil	25,000 – 40,000
Nitrogen oxides		90 – 450
Particulate matter		60 – 150
Sulfur oxides		60 – 300
Volatile organic compounds		120 - 300
Solid waste		20 - 100

Notes:
1. Based in part on EC BREF for Refineries

2.2 Occupational Health and Safety

Occupational Health and Safety Guidelines

Occupational health and safety performance should be evaluated against internationally published exposure guidelines, of which examples include the Threshold Limit Value (TLV[®]) occupational exposure guidelines and Biological Exposure Indices (BEIs[®]) published by American Conference of

Governmental Industrial Hygienists (ACGIH),¹⁴ the Pocket Guide to Chemical Hazards published by the United States National Institute for Occupational Health and Safety (NIOSH),¹⁵ Permissible Exposure Limits (PELs) published by the Occupational Safety and Health Administration of the United States (OSHA),¹⁶ Indicative Occupational Exposure Limit Values published by European Union member states,¹⁷ or other similar sources.

Accident and Fatality Rates

Projects should try to reduce the number of accidents among project workers (whether directly employed or subcontracted) to a rate of zero, especially accidents that could result in lost work time, different levels of disability, or even fatalities. Facility rates may be benchmarked against the performance of facilities in this sector in developed countries through consultation with published sources (e.g. US Bureau of Labor Statistics and UK Health and Safety Executive)¹⁸.

Occupational Health and Safety Monitoring

The working environment should be monitored for occupational hazards relevant to the specific project. Monitoring should be designed and implemented by accredited professionals¹⁹ as part of an occupational health and safety monitoring program. Facilities should also maintain a record of occupational accidents and diseases and dangerous occurrences and accidents. Additional guidance on occupational health and safety monitoring programs is provided in the **General EHS Guidelines**.

¹⁴ <http://www.acgih.org/TLV/>¹⁴ Available at: <http://www.acgih.org/TLV/> and <http://www.acgih.org/store/>

¹⁵ Available at: <http://www.cdc.gov/niosh/npg/>

¹⁶ Available at: http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARD&p_id=9992

¹⁷ Available at: http://europe.osha.eu.int/good_practice/risks/ds/oe/

¹⁸ Available at: <http://www.bls.gov/iif/> and <http://www.hse.gov.uk/statistics/index.htm>

¹⁹ Accredited professionals may include Certified Industrial Hygienists, Registered Occupational Hygienists, or Certified Safety Professionals or their equivalent.

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Annex A: General Description of Industry Activities

The EHS Guidelines for Petroleum Refining cover processing operations from crude oil to finished liquid products, including liquefied petroleum gas (LPG), Mo-Gas (motor gasoline), kerosene, diesel oil, heating oil, fuel oil, bitumen, asphalt, sulfur and intermediate products for the petrochemical industry (e.g. propane / propylene mixtures, virgin naphtha, middle distillate and vacuum distillate). Finished products are produced from the blending of different intermediate products. These blends are normally referred as gasoline pool, diesel oil pool, LPG pool, among others, and have varying compositions dependent on the configuration of the refinery process.

Petroleum refineries are complex systems specifically designed based on the desired products and the properties of the crude oil feedstock. Refineries may range from medium integrated refineries to fully integrated refineries (or total conversion refineries), based on the use of different processing units.

The refinery feedstock is crude oil, which is a mixture of hydrocarbon compounds.²⁰ The hydrocarbons in crude oil are a mixture of three chemical groups including paraffins (normal and isoparaffins), naphthenes, and aromatics. The most common distinction between crude oil types is 'sweet' or 'sour'. Sweet crude oil is normally low in sulfur and lightly paraffinic. Sour crude oil is usually high in sulfur (more than 0.5 wt percent) and heavily naphthenic. Crude oils are also classified into light, medium and heavy, dependent on their content of paraffins, naphthenics, and aromatics.

²⁰ The hydrocarbon mixture may involve different chemical composition and molecular structures with some impurities. Most of these impurities, such as sulfur (largely in the form of organic compounds such as mercaptans and sulfides), nitrogen, vanadium and nickel are chemically bound to the hydrocarbon structures. Others, such as sand/clay, water and water-soluble salts of zinc, chromium and sodium are present as inorganic material.

Process Units

Desalting

Desalting is a process to wash the crude oil with fresh water at high temperature and pressure to dissolve, separate and remove the salts and solids. Crude oil and/or reduced crude (commonly referred as oily feedstock) and fresh water are the inputs to the Desalting Unit, and washed crude oil and contaminated water are its outputs.

Primary Distillation Units

These units include the Atmospheric Distillation Unit (Topping or CDU) followed by Vacuum Unit (HVU). Desalted crude oil is fed to a distillation tower working at atmospheric pressure where the various fractions composing the crude oil are separated according to their boiling range. The heaviest fractions recovered at CDU bottom (atmospheric residue) do not vaporize under the tower atmospheric pressure, and require further fractionation under vacuum conditions in the vacuum distillation tower.

Bitumen Production Unit

The Bitumen Production Unit is fed with vacuum residue. In the Bitumen Blowing Unit (BBU), air is blown into hot bitumen, which causes dehydrogenation and polymerization reactions and yields a harder product with higher viscosity, a higher softening point and reduced penetration. The blown bitumen is removed from the bottom of the oxidation vessel and cooled before being sent to storage. Bitumen is typically stored in heated, insulated and nitrogen blanketed cone roof tanks fitted with safety valves. The nitrogen discharged into the atmosphere may contain hydrocarbons and sulfur compounds in the form of aerosol-containing liquid droplets.

Hydrogen Consuming Processes

Hydrotreating²¹ and hydro-processing processes are used to remove impurities such as sulfur, nitrogen, oxygen, halides and traces of metal impurities that may deactivate the noble metals catalysts. Hydrotreating also upgrades the quality of the processed fractions by converting olefins and di-olefins into paraffins for the purpose of reducing gum formation in fuels. Hydroprocessing cracks heavy molecules into lighter, more saleable products. Both processes are usually placed upstream of process units, such as the Catalytic Reforming Unit and the Hydrocracking Units,²² in which sulfur and nitrogen could have adverse effects on catalyst operation. Hydrogen consumption is high and requires the presence of a Hydrogen Plant in the refinery.

The C₅ – C₆ isomerization units are based on skeletal isomerization processes (e.g. 'once-through' and 'recycle' types), used to convert a linear molecule into a branched one with the same raw formula. Typically, low molecular weight normal paraffins (C₄-C₆) are converted into isoparaffins which have a much higher octane index. There are three distinct different types of catalysts currently in use, including chloride promoted catalysts, zeolites, and sulfated zirconium catalysts.

The Dienes Hydrogenation and Butylenes Hydroisomerization Unit is placed upstream of the alkylation and based on a highly

selective catalytic process. This process hydrogenates acetylenes and dienes into the corresponding mono-olefins without affecting the valuable olefin content of the feedstock, while converting linear butene-1 into linear butenes -2 which in alkylation leads to higher octane gasoline components than those derived from butene-1.

Pretreating and Catalytic Reformer Unit

The typical feedstocks are heavy virgin naphtha (HVN) from the crude distillation unit and, when applicable, the hydrotreated heavy naphtha from the hydrocracker unit. Naphtha feed, mixed with a hydrogen-rich gas stream, is heated and vaporized and then fed into the hydrotreater reactor (pretreating), which contains a fixed bed of cobalt / nickel / molybdenum catalyst. The C₅-minus hydrocarbons contained in the product, after the separation of hydrogen, are removed in a stripping tower. The heavy naphtha, free from nitrogen and sulfur compounds, leaving the hydrotreating section, enters the Catalytic Reformer Section to be upgraded for use as high octane gasoline blend-stock.

There are four major types of reactions which occur during the reforming process: (1) dehydrogenation of naphthenes to aromatics; (2) dehydrocyclization of paraffins to aromatics; (3) isomerization; and (4) hydrocracking. There are several catalytic reforming processes in use and they can be classified into three categories including 'continuous', which makes use of moving bed reactors, as well as 'cyclic' and 'semi-regenerative', both making use of fixed bed reactors.

Catalytic Cracking Units (Catcrackers)

Catalytic Cracking is by far the most widely used conversion process to upgrade heavy hydrocarbons into more valuable lower boiling hydrocarbons. It makes use of both heat and catalyst to break the large hydrocarbon molecules into smaller, lighter molecules. Unlike the hydrocracker unit, no hydrogen is used and, consequently, limited desulfurization takes place

²¹ The hydrotreating process can be divided into a number of reaction categories: naphtha hydrotreating (or pretreating, where upstream of reforming), hydrodesulfurization (HDS, including Middle Distillate Hydrodesulfurization Unit, Selective Catalytic Hydrodesulfurization, and Diesel Oil Deep Hydrodesulfurization), selective hydrocracking (or dewaxing), hydrodenitrication, saturation of olefins and saturation of aromatics, residue hydrotreating.

²² The Hydrocracking Unit is one of the most versatile of all refining processes, capable of converting any fraction, from atmospheric gas oils to residual (de-asphalted) oil, into products with a molecular weight lower than that of the feed. The Hydrocracking reactions occur under high hydrogen partial pressure in catalytic reactors at a substantially high pressure (35 to 200 bar) and at temperatures between 280 and 475°C. The catalyst (Co/Ni/Mo based) has a two-fold function: hydrogenation and cracking. The most common types of reactor technologies applied are Fixed Bed and Ebullated Bed. The selection of the type of technology is predominantly determined by the metal content in the feed.

during the process. Catalytic cracking designs include moving-bed reactors, fluidized-bed reactors (e.g. Fluid Catalytic Cracking Unit [FCCU], Residue Catalytic Cracking Unit [RCCU]), and once-through units. FCCU feed stream is the desulfurized heavy vacuum gasoil coming from hydrocracking. RCCU treats heavier feedstocks, such as the atmospheric distillation residue.

In both processes, oil and vapor are contacted with hot catalyst in the 'Riser Reactor'. The cracking process takes place in presence of a zeolite type catalyst. The fluidized catalyst and the reacted hydrocarbon vapor separate mechanically in a cyclone system and any oil remaining on the catalyst is removed by feeding steam in the stripping section of the reactor. The catalytic cracking processes produce coke. This is deposited on the catalyst surface, thereby reducing activity and selectivity. Catalysts should be continuously regenerated, essentially by burning off the coke from the catalyst at high temperature in the regenerator. Products are separated by means of a fractionation train.

Gas Plant Units

Low boiling hydrocarbons are usually treated in a common separation plant operating at elevated pressure. Gas plants allow recovery and separation by distillation of C1 - C5 hydrocarbons and higher compounds from the various refinery off-gases. The Gas Plant consists of a fractionation train where the following streams are separated: C1-C2 fraction; C3 fraction (propane); C4 fraction (butane); and debutanized gasoline. Amine Treating Units remove hydrogen sulfide and carbonyl sulfide from all product streams. Before being sent to the relevant storages, liquid products pass through to Sweetening Units based on selective adsorption on molecular sieves.

Etherification Units

The feedstocks of MTBE/ETBE units are the C4 hydrocarbons stream coming from the FCCU, and methanol or ethanol.

Isobutylene reacts with methanol or ethanol to yield directly MTBE (methyl-tert-butyl-ether) or ETBE (ethyl-tert-butyl-ether), respectively. The reactors can be of adiabatic or tubular type or combined with a fractionation tower (this type of reactor is normally referred as Catalytic Distillation Reactor or Reactor Column). The catalyst is a sulfonic resin. The feedstock of TAME units is LCN, (composed of C₅ hydrocarbons, both paraffins and olefins). However, only the reactive isoamylenes (2-methyl-butene-1 and 2-methyl-butene-2) react with methanol to directly yield TAME (tert-amyl-methyl-ether). Adiabatic type reactors are used, and the catalyst is the same as for the MTBE / ETBE Units.

Alkylation Units

The purpose of the alkylation unit is to produce a high-quality gasoline blending component called alkylate. Alkylation is the reaction of C₃ and C₄ olefins with isobutane to form higher molecular-weight isoparaffins with high octane number (preferably iso-octane). The process involves low-temperature reaction conditions conducted in the presence of very strong acids (hydrofluoric acid or non fuming sulfuric acid). The reaction in hydrofluoric acid alkylation produces acid soluble oil (normally referred as ASO) which, after neutralization, is burned in a furnace by means of a dedicated burner. The reaction in sulfuric acid alkylation produces acid sludges (spent acid), which are burned to recover sulfuric acid (sulfuric acid regeneration).

The acid sludges are fed into a decomposition furnace together with fuel gas, where, at 1,050°C, the decomposition of the sulfuric acid into sulfur dioxide takes place. The gas leaving the furnace is cooled down to 350°C in a waste heat boiler, and then further cooled and filtered. The gas and condensed water are fed to the gas treatment system.

Polymerization Unit

In polymerization process unit, the C3 and C4 olefins are dimerized and oligomerized to produce the so called polymeric gasoline as high octane blending component. The process is similar to alkylation in its feed and products, but is often used as a less expensive alternative to alkylation. The reactions typically take place under high pressure in the presence of a phosphoric acid catalyst adsorbed onto natural silica.

Coking Units

Coking is a severe thermal cracking process used primarily to reduce refinery production of low-value residual fuel oils and transform them into transportation fuels, such as gasoline and light and heavy gas oils. As a part of the process, coking also produces petroleum coke, which is essentially solid carbon, with varying amounts of impurities and containing 5–6 percent hydrocarbons. Two types of coking processes exist: the delayed coking and the fluid coking processes. The flexi-coking process is similar to fluid coking, but has fully integrated gasification suitable to gasify the fluidized coke in order to produce coke gas.

The hot vapors from the coke drums contain cracked lighter hydrocarbon products, hydrogen sulfide and ammonia, and are fed back to the fractionator where these lighter hydrocarbon products can be treated in a sour gas treatment system. The condensed hydrocarbons are reprocessed, whereas water is re-used for coke drum quenching or cutting.

The sulfur contained in the coke is converted in flexicoking gasifiers, primarily into hydrogen sulfide, and into traces of carbonyl sulfide. The nitrogen contained in the coke is converted into ammonia.

Visbreaking Unit

The Visbreaking Unit is a well-established non catalytic thermal cracking process that converts atmospheric or vacuum residues

to gas, naphtha, distillates and tar. It uses heat and pressure to break large hydrocarbon molecules into smaller lighter molecules.

The most important factor in controlling the cracking severity should always be the stability and the viscosity of the so called visbroken residue, which is fed to the fuel oil pool. In general, an increase in the temperature in or residence time results in an increase in cracking severity. Increased severity increases gasoline yield and, at the same time, produces cracked residue (fuel oil) of lower viscosity. Excessive cracking, however, leads to an unstable fuel oil, resulting in sludge and sediment formation during storage.

There are two types of visbreaker operations: coil or furnace cracking and soaker cracking. The gas produced is fed to an amine treating unit, to remove hydrogen sulfide.

Lube Oil Production Units

A base oil complex typically consists of a vacuum distillation tower, a deasphalting unit, an aromatic extraction unit, a dewaxing unit, an optional high pressure hydrogenation unit and a hydrofinishing unit to improve color and stability, to meet product specifications and to remove impurities. A conventional base oil complex is very labor intensive, mainly due to its batch operation, the many grades of base oil normally produced and the associated intensive product handling operations.

Gas Treatment and Sulfur Recovery Units

Sulfur is removed from a number of refinery process off-gas streams (sour gas) in order to meet the SO_x emission limits and to recover saleable elemental sulfur. Process off-gas streams, or sour gas, from the coker unit, FCCU, hydrotreating units and hydroprocessing units, contain high concentrations of hydrogen sulfide and carbonyl sulfide mixed with light refinery fuel gases. Before elemental sulfur is recovered, the fuel gases (primarily methane and ethane) need to be separated from hydrogen

sulfide and carbonyl sulfides. This is typically accomplished by dissolving hydrogen sulfide and carbonyl sulfides in a chemical solvent. The solvents most commonly used are amines, such as diethanolamine (DEA). Dry adsorbent, such as molecular sieves, activated carbon and iron sponge are also used.

In the amine solvent processes conducted in the amine gas treating units, DEA solution, or another amine solvent, is pumped to an absorption tower where the gases are contacted and hydrogen sulfide and carbonyl sulfide are dissolved in the solution. The fuel gases, free from hydrogen sulfide and carbonyl sulfide, are removed and sent to refinery fuel gas network. The amine-hydrogen sulfide and carbonyl sulfide solution is regenerated by heating and steam stripping to remove the hydrogen sulfide gas before recycling back to the absorber. Hydrogen sulfide and carbonyl sulfide are sent to the Claus Unit for sulfur recovery. Air emissions from sulfur recovery units will consist of hydrogen sulfide, SO_x, and NO_x in the process tail gas, as well as fugitive emissions.

The Claus process consists of the partial combustion of the hydrogen sulfide and carbonyl sulfide-rich gas stream and then of reacting the resulting sulfur dioxide and unburned hydrogen sulfide in the presence of a bauxite catalyst to produce elemental sulfur. Claus units remove only 90 percent of hydrogen sulfide and carbonyl sulfide, and are followed by other processes to complete sulfur removal (up to 99.5 percent).

Sour Water Stripper Unit (SWSU)

Many process units generate sulfides and ammonia-contaminated water, normally referred as sour water. Sour Water Stripper Unit (SWSU) permits reusing sour water by removing sulfides and ammonia. The process operation is complicated by the presence of other chemicals, such as phenol, and cyanides.

Hydrogen Plant

Normally the feedstock the hydrogen plant is the methane obtained by the refinery process units, LPG, or refinery external natural gas, if available. This unit normally consists of a reformer and produces a hydrogen – carbon monoxide mixture, referred as synthetic gas (syngas). After passing through a heat recovery section, cold syngas enters the shift conversion reactor where, under an iron or copper based catalyst, carbon monoxide is reacted with water to yield more hydrogen and carbon dioxide. The latter is separated in an amine absorption – regeneration unit. A closed drain system collects and recovers any amine drains and spills, thereby preventing them from being purged into the WWTU.

Chemical Treatment Units

Chemical treatments are used to achieve certain product specifications. The Extraction Sweetening Units are designed to reduce the mercaptans content of hydrocarbon streams to mitigate odor nuisance and to reduce corrosivity. These treatments are accomplished by either extraction or oxidation or both, depending on the treated process stream. The extraction process removes the mercaptans by caustic extraction, resulting in a lower sulfur content. The sweetening process causes the mercaptans to be converted into less odorous and less corrosive disulfides which remain in the product. As a result, no reduction in the total sulfur content takes place during sweetening and, consequently, it is only applied to those streams where sulfur content is not a problem.

The spent caustic scrubbing liquor (spent caustic) coming from the Extraction Unit is one of the most problematic waste streams generated in refineries. This is primarily due to the very high sulfides concentration which make it non suitable for direct discharge into the WWTU. High levels of sulfides can also create odor and safety problems when released as gas.

In the Caustic Oxidation Unit, the reactive sulfides contained in the spent caustic liquor are oxidized into soluble thiosulfates, sulfites and sulfates. The treated stream is then suitable for biotreatment in the WWTU.

Gasification Units

The gasification units include Coke Gasification, Hydrocarbons Gasification (Partial Oxidation), and Hydrogen Purification (i.e., Wet Scrubbing, Membrane Systems, Cryogenic Separation and Pressure-Swing Adsorption). The synthetic gas produced by coke gasification contains hydrogen sulfide and carbonyl sulfide, and the gas is treated in an Amine Treating Unit.

Blending Facilities

Blending is the final operation in petroleum refining. It consists of mixing the products in various proportions to meet commercial specifications. Blending can be carried out in-line or in batch blending tanks.

Air emissions from blending include fugitive VOC from blending tanks, valves, pumps and mixing operations.

Auxiliary Facilities

Auxiliary facilities at petroleum refineries typically consist of waste water treatment units, blow down and flare systems, vapor recovery units (e.g. thermal oxidation, absorption, adsorption, membrane separation and cryogenic condensation), and energy/electricity systems (e.g. boilers, furnaces, gas turbines).