

ENVIRONMENTAL, HEALTH, AND SAFETY GUIDELINES FOR PETROLEUM REFINING

INTRODUCTION

1. 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/ehsguidelines.

2. 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.

3. 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. The applicability of specific technical recommendations should be based on the professional opinion of qualified and experienced persons.

4. 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

5. The **EHS Guidelines for Petroleum Refining** cover processing operations from raw crude oil to finished products, for example refinery fuel gas, liquefied petroleum gas (LPG), motor gasoline (Mo-Gas), kerosene, diesel oil, heating oil, fuel oil, bitumen, asphalt, lubricant oils, waxes, sulfur, pet-coke, and intermediate products (e.g., propane/propylene mixtures, virgin naphtha, middle distillate and vacuum distillate, aromatics) for the petrochemical industry. Annex A contains a description of industry activities.

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.

Further information on EHS issues related to storage tank farms is provided in the **EHS Guidelines for Crude Oil and Petroleum Product Terminals**.

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1. INDUSTRY-SPECIFIC IMPACTS AND MANAGEMENT

6. The following section provides a summary of the EHS issues that may arise during the operational phase of petroleum refining, 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 Environment

7. Environmental issues associated with petroleum refining include the following:
- Emissions to atmosphere;
 - Handling and disposal of process wastewater (storage, transportation, and treatment);
 - Handling of hazardous materials and wastes; and
 - Noise from operating machinery.

Emissions to Atmosphere

Flue Gases

8. Flue gas emissions to the atmosphere of carbon dioxide (CO₂), nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), and particulate matter (PM) in the petroleum refining sector result from the combustion of gas and oil in gas turbines, boilers, engines, and process heaters for power, steam, and heat generation. Flue gas can also be emitted from waste heat boilers associated with some process units during continuous catalyst regeneration (CCR) or fluid petroleum coke combustion. For example, flue gas is emitted from the stack to the atmosphere in the Bitumen Blowing Unit (BBU), from the catalyst regenerator in both the Fluid Catalytic Cracking Unit (FCCU) and the Residue Catalytic Cracking Unit (RCCU), and in the sulfur recovery unit (SRU), possibly also containing small amounts of SO_x and hydrogen sulfide (H₂S).

9. 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 such as boilers, engines, and turbines with a capacity greater than 50 MWth, refer to the **EHS Guidelines for Thermal Power Plants**.

10. For process heaters, the following primary pollution prevention and control measures should be considered:

- Installation of combustion air preheaters, to increase furnace efficiency;
- Optimization of furnace operations, and hence combustion efficiency, by continuous monitoring and advanced control of the operations variables (temperature and oxygen concentration of flue gas for combustion optimization air/fuel ratio for the fuel mix; optimizing excess air to minimize heat losses via unburned gases or unburned residues);
- High-thermal-efficiency heater designs with good control systems (e.g., oxygen trim);
- Prevention of the condensation of exhaust gas on surfaces;
- Minimization of power requirements by use of high-efficiency pumps, fans, and other equipment;
- Techniques to control CO emissions, such as good operation and control, constant delivery of liquid fuel in the secondary heating, good mixing of the exhaust gases, and catalytic afterburning;
- Regular cleaning of heating surface (soot blowing) for liquid fuel or mixed firing; and
- High-emissivity refractories for radiant heat transfer improvement, e.g., by application of ceramic coatings as reflecting surfaces.

Venting and Flaring

11. Venting and flaring are important operational and safety measures used in petroleum refining facilities, particularly during non-routine operational periods such as malfunction or upset, as a means of safely disposing of vapors. Hydrocarbons are emitted from emergency process vents and safety valve discharges. These are collected in the blow-down network that is flared.

12. For planned start-up and shutdown, a flare gas recovery system should be used. During non-emergency releases, excess gas from process vents should be recovered or controlled and the volume of gas to be flared should be minimized.

13. Flaring modifies, by means of combustion, the chemical nature of the emitted substances (e.g., the combustion of H₂S generates sulfur dioxide (SO₂), while the combustion of hydrocarbon generates CO₂ plus water vapor). Monitoring of gas emissions should encompass both the concentration of pollutants at ground level as well the total quantity of pollutants released annually. Before flaring is adopted, feasible alternatives for the use of the gas should be evaluated and—where practical, reasonable, and safe—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 activities should be recorded. Flare management plans should be prepared and implemented.²

² Such as; U.S. EPA, 40 CFR 60 Standard of Performance for New Stationary Sources- Subpart Ja (2015).

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

- Implementing source gas reduction measures to the maximum extent possible;
- Using efficient flare tips (i.e., optimal released gas sonic velocity, in order to avoid malfunctioning of the flare due to its flame off), and optimization of the size and number of burner nozzles (not less than three, which will ensure—acting as pilot burners, positioned 120° from each other—the continuity of flaring);
- 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 the installation of purge gas reduction devices, flare gas recovery units (mainly for continuous or predictable releases), an upstream knock-out drum (vapor–liquid separator used to avoid entrainment of liquid to the flare stack), soft-seat valve technology (where appropriate), conservation pilots, the use of inert purge gas, and the diversion of flows into the refinery fuel gas distribution network;
- Minimizing the risk of pilot blow-out by ensuring sufficient exit tip velocity and providing wind guards;
- Using a reliable pilot auto-ignition system;
- Installing high-integrity instrument pressure protection systems, where appropriate, to reduce over-pressure events and avoid or reduce flaring situations;
- Minimizing liquid carry-over and entrainment in the gas flare stream with a suitable liquid separation system;
- Minimizing flame lift (flash off) and flame lick (flash back);
- Operating flares to control odor and visible smoke emissions using suitable optical instruments, such as flame detectors, which act on the steam injection in case of black smoke at tip;
- Locating flares at a safe distance from local communities and the workforce, including workers' accommodation units;
- Implementing burner maintenance planning and replacement programs to ensure continuous maximum flare efficiency;
- Metering flare gas on a monthly basis in the interest of pollution evaluation, mainly in terms of CO₂ and SO₂, as well as of released heat (which is an indirect estimation of the greenhouse gas (GHG) emissions);
- Avoiding over-steaming, as too much steam in a flare will reduce flare performance;
- Avoiding a wake-dominated flame. A strong crosswind at high velocity can have a powerful effect on the flare's flame dimensions and shape, causing the flame to be wake-dominated (i.e., the flame is bent over on the downwind side of a flare and imbedded in the wake of the flare tip), reducing flare performance and potentially damaging the flare tip; and
- Avoiding flame lift-off, a condition in which a flame separates from the tip of the flare and there is space between the flare tip and the bottom of the flame due to excessive air induction as a result of the flare gas and center steam exit velocities. This type of flame can reduce flare performance and can progress to a condition where the flame becomes completely extinguished.

15. To minimize flaring events as a result of equipment breakdowns and plant upsets, plant reliability should be high (>95 percent). Provisions should be made for taking equipment offline for planned maintenance regimes and plant turnaround protocols, to the extent that the refinery does not exceed 8,000 operating hours/year (corresponding to one month/year of refinery-planned shut-down for general maintenance). This means achieving a Refinery Service Factor of 91 percent (or 8,000 operating hours/24 hours per day x 365 days= 0.91).

Fugitive Emissions

16. Fugitive emissions in petroleum-refining facilities may occur from leaking tubing, valves, connections, flanges, gaskets, steam traps, packing, open-ended lines, floating roof storage tanks and pump seals, gas conveyance systems, compressor seals, pressure relief valves, breathing valves, tanks or open pits/containments, oil-water separators, and in the storage, loading, and unloading operations of hydrocarbons. Depending on the refinery process scheme, fugitive emissions may comprise:

- 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 semi-VOCs;
- Inorganic gases, including ammonia (NH₃), CO, CO₂, SO₂ and sulfur trioxide (SO₃) from sulfuric acid regeneration in the sulfuric acid alkylation process, NO_x, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), t-amylmethyl ether (TAME), methanol, and ethanol; and
- If occurring, hydrofluoric acid (HF) from hydrogen fluoride alkylation and H₂S.

17. There is significant potential for VOC emissions from cone-roof storage tanks during loading due to fugitive releases from the out-breathing valves; fugitive emissions of hydrocarbons through the 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. It is also possible for nitrogen to be emitted from bitumen storage tanks and possibly saturated with hydrocarbons and sulfur compounds at storage temperature (150–180°C) in the form of aerosols. Other potential fugitive emission sources include the vapor recovery unit vents and gas emissions from caustic oxidation.

18. Recommendations to prevent and limit fugitive emissions include the following:

- A structured leak detection and repair (LDAR) program should be implemented; based on a systematic review of Process and Instrumentation Diagrams (P&IDs), this program should identify streams and equipment (e.g., pipes, valves, seals, tanks, and other infrastructure components) where fugitive VOC emissions are a possibility (through component degradation, for example) and prioritize their monitoring with vapor detection equipment, followed by maintenance or replacement of components, as needed.

- When selecting appropriate valves, packings, flanges, fittings, and seals, consideration should be given to their effectiveness to reduce gas leaks and fugitive emissions.³
- To minimize their release to the atmosphere, hydrocarbon vapors should be either contained (e.g., using a nitrogen blanketing system, an internal floating roof for tanks, or a cover system for separator) or routed back to the process.
- Installing a Vapors Recovery Unit, in lieu of open venting or flaring. 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, loading racks).
- The incineration of gas should be conducted at a high temperature (approximately 800°C) to ensure complete destruction of minor components (e.g., H₂S, aldehydes, organic acids, and phenolic components) and to minimize emissions and odor impacts.
- With regard to emissions from HF, alkylation plant vents should be collected and neutralized for HF in a scrubber before being sent to flare.
- With regard to naphtha, gasoline, methanol/ethanol, and ethers—including MTBE, ETBE, and TAME—loading/unloading racks should be provided with vapor controls, e.g. 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**.

Nitrogen Oxides

19. NO_x may be emitted from boilers, process heaters, furnaces, Combined Heat Power (CHP) units, gas turbines, fluid catalytic cracking (FCC) regenerators, as well as flare and other process and combustion units. NO_x formation arises from three mechanisms: fuel NO_x (due to nitrogen content in the fuel), thermal NO_x (due to nitrogen in the air under high temperatures and excess air conditions during combustion), and prompt NO_x (due to the reaction of atmospheric nitrogen (N₂) with free radicals such as C, CH, and CH₂ fragments derived from fuel in the earliest stage of combustion). To reduce NO_x emissions, low-NO_x burners are the most commonly installed technology on combustion devices, while controlling NO_x emissions associated with FCCs typically involve the consideration of selective catalytic reduction (SCR) or thermal de-NO_x technologies.

20. The ammonia (NH₃) formed during the naphtha and gasoil hydrodesulfurization process is fed as a component of the sour feed gas to the thermal reactor of the SRU and converted to fuel NO_x. In addition, thermal NO_x is formed at the SRU due to high-temperature (approximately 1,400°C) oxidation of nitrogen from the process air.

21. In addition to the guidance for the management of these issues presented in the **General EHS Guidelines**, recommended pollution prevention and minimization measures include High-Temperature Air Combustion (HiTAC), otherwise called flameless (or colorless) combustion. It can be used in SRUs, especially those employing lean acid gas streams, which cannot be burned without the use of auxiliary fuel or oxygen enrichment under standard conditions. With the use of HiTAC, lean acid gas streams can be burned with uniform thermal fields without the need for fuel enrichment or oxygen addition. The uniform

³ European Commission (EC) Joint Research Center (JRC), Best Available Techniques Reference (BREF) Document for the Refining of Mineral Oil and Gas (2015).

temperature distribution favors clean and efficient burning, with an additional advantage of significant reduction of NO_x, CO, and hydrocarbon emission.

Sulfur Oxides

22. Sulfur oxides (SO_x) and H₂S may be emitted from boilers, heaters, and other process units (such as SRUs, FCC regenerators, flares, wastewater stripping, incondensable off-gas incinerators, decoking operations, and coke calcinations). Emissions will vary according to the sulfur content of the processed crude oil, the sulfur content of the fuel that is being combusted, the degree of sulfur recovery, and the level of SO_x emission controls. Sulfur dioxide (SO₂) and sulfur trioxide (SO₃) may be emitted from sulfuric acid regeneration in the sulfuric acid alkylation process. In refinery off gases, SO₂ may have pre-abatement concentration levels of 1,500–7,500 milligrams per cubic meter (mg/m³).⁴

23. To reduce SO_x emissions and improve product quality, sulfur-bearing refinery streams are typically directed to hydrotreating units where hydrogen combines with sulfur to form H₂S; this, in turn, is directed to the Amine Unit, from which a single stream, at high H₂S concentration, is sent to the SRU, generally based on the Claus process.⁵

24. 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 SRUs (e.g., Claus units, equipped with the specific section of Tail Gas Treatment (TGT)).⁶
- Install scrubbers with caustic soda solution to treat flue gases (caustic wash of acid gas stream, to remove acids) from the alkylation unit absorption towers.

Particulate Matter

25. Particulate emissions from refinery units are associated with flue gas from furnaces and boilers; catalyst fines emitted from fluidized catalytic cracking regeneration units and other catalyst-based chemical processes; the handling of pet-coke; fines and ash generated during incineration of sludge; and decoking and soot blowing off furnaces and flares. Particulates may contain metals (e.g., vanadium, nickel). Condensable PM_{2.5} (e.g., nitrates, sulfates) are another type of particulate emissions. Measures to control particulates may also contribute to control of metal emissions from petroleum refining.⁷

26. Recommended pollution prevention and minimization measures include the following:

- On large sources of particulate matter emissions such as FCCU regeneration units and sludge incinerators, install high-efficiency air pollution control devices (e.g., bag filters, electrostatic

⁴ EC European Integrated Pollution Prevention and Control Bureau (EIPPCB), Best Available Techniques (BAT) Reference Document for Refineries (2003).

⁵ See Annex A: General Description of Petroleum Industry Activities.

⁶ 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.

⁷ EC JRC, Best Available Techniques Reference (BREF) Document for the Refining of Mineral Oil and Gas (2015).

precipitators, scrubbers, third-stage cyclones). Consider these technologies along with NO_x and SO_x emissions control technologies (e.g., wet gas scrubbers) if PM_{2.5} control is warranted. A combination of these techniques may achieve >99 percent abatement of particulate matter.

- Implement particulate emission reduction techniques during coke handling, including:
 - Store (green sponge) pet-coke in bulk under enclosed shelters;
 - Keep coke constantly damp;
 - Cut coke in a crusher and convey it to an intermediate storage silo (hydrobins);
 - Spray coke with a fine layer of gasoil, to stick the dust fines to the coke;
 - Use covered conveyor belts with extraction systems to maintain a negative pressure;
 - Use aspiration systems to extract and collect coke dust; and
 - Pneumatically convey the fines collected from the cyclones into a silo fitted with exit air filters, and recycle the collected fines to storage.
- Consider fuel switching, e.g., replace heavy fuel oil with light fuel oil, natural gas, or refinery gas.

Greenhouse Gases

27. Carbon dioxide (CO₂) and methane (CH₄) are the primary greenhouse gases (GHGs) emitted by the petroleum refining industry and may be produced in significant amounts during petroleum refining and related combustion processes. Carbon dioxide and other gases (e.g., N₂O) may be discharged to the atmosphere during the in-situ catalyst regeneration of noble metals. Aggregate GHG emissions should be quantified annually in accordance with internationally recognized methodologies.

28. Operators should include at the design stage or when considering major revamping improvements enhancement to stationary combustion sources (i.e., steam generation boilers, process heaters, combined heat and power), upgrading fuel gas systems and flares, and installing power/waste heat recovery units to minimize GHG emissions. The overall objective should be to reduce GHG emissions and evaluate cost-effective options for reducing emissions that are technically feasible.⁸ 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

29. Significant volumes of wastewaters in petroleum refining include “sour” process wastewater and non-oily/non-sour process wastewater. Sour wastewater is generated from desalting, topping, vacuum distillation, pretreating, light- and middle-distillate hydrodesulfurization, hydrocracking, catalytic cracking, coking, and visbreaking/thermal cracking. Sour wastewater may be contaminated with hydrocarbons, H₂S, NH₃, organic sulfur compounds (R-S-H mercaptans), organic acids, and phenol. Process wastewater that is high in H₂S and/or NH₃ is treated in the Sour Water Stripper Unit (SWSU) to remove these and other

⁸ Detailed information on energy efficiency opportunities for petroleum refineries is presented in University of California, “Energy Efficiency Improvement and Cost Saving Opportunities for Petroleum Refineries” (2005) <http://repositories.cdlib.org/cgi/viewcontent.cgi?article=3856&context=lbnl>; and in U.S. EPA, “Available and Emerging Technologies for Reducing Greenhouse Gas Emissions from the Petroleum Refining Industry” (2010).

compounds, before recycling for internal process uses, or before final treatment and disposal through an on-site wastewater treatment unit. Non-oily/non-sour process wastewater has the potential to cause wastewater treatment plant (WWTP) disturbances. Boiler blowdown and demineralization plant reject streams have the undesirable potential to extract phenolic compounds from the oil phase into the water phase, as well as cause emulsions in the WWTP if incorrectly neutralized. Liquid wastewater may also result from accidental releases or leaks of small quantities of products from process equipment, machinery, and storage areas/tanks. Treated sour water is typically returned to the SWSU for stripping, rather than being sent to a refinery's wastewater treatment plant.

30. Recommended process wastewater management practices include:

- Prevention and control of accidental releases of liquids through regular inspections and maintenance of storage 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 capacity for storing process fluids to enable maximum recovery into the process and, as a consequence, avoiding large discharges of process liquids into the oily wastewater drainage system;
- Design and construction of wastewater and hazardous materials storage containment basins with suitably impervious surfaces to prevent infiltration of contaminated water into soil and groundwater;
- Segregation of process wastewater from storm water and segregation of wastewater and hazardous materials containment basins; and
- Implementation of good housekeeping practices, including conducting product transfer activities over paved areas and prompt collection of small spills.

31. 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 to the wastewater treatment system following caustic oxidation.
- Direct spent caustic liquor from 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 responsive to biological treatment and should be prevented from entering and adversely affecting the wastewater treatment system.
- If present at the facility, acidic and caustic wastewater 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 wastewater, as well as blowdown from cooling water towers, may contain additives (e.g., biocides) that may require treatment in the WWTP prior to discharge.
- Hydrocarbon-contaminated water from scheduled cleaning activities during facility turnaround and hydrocarbon-containing wastewaters from process leaks should be treated in the WWTP.

Process Wastewater Treatment

32. 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, oil skimmers, Coalescing Plate Separators (CPS), Dissolved Air Flotation (DAF) 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 the reduction of soluble organic matter, measured as Biological Oxygen Demand (BOD);
- Chemical or biological nutrient removal for reduction of nitrogen and phosphorus;
- Chlorination of wastewater when disinfection is required; and
- Dewatering and disposal of residuals in designated hazardous waste landfills.

33. 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 Chemical Oxygen Demand (COD) using activated carbon or advanced chemical oxidation; (iii) reduction in wastewater toxicity using appropriate technology (such as reverse osmosis, ion exchange, activated carbon); and (iv) containment and neutralization of nuisance odors.

34. Management of industrial wastewater and examples of treatment approaches are discussed in the **General EHS Guidelines**. Through the 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

35. Guidance on the management of non-contaminated wastewater from utility operations, non-contaminated storm water, 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**.

36. 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 generally added to the fresh water to prevent internal corrosion and to highlight leaks. In managing hydro-test waters, the following pollution prevention and control measures should be implemented:

- Use the same water for multiple tests;
- Reduce the need for corrosion inhibitors and other chemicals by minimizing the time that test water remains in the equipment or pipeline; and
- If chemical use is necessary, select effective chemicals with the lowest toxicity, bioavailability, and bioaccumulation potential, and with the highest biodegradability.

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

Handling of Hazardous Materials

38. 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

39. There are numerous larger-volume wastes, both hazardous and non-hazardous, generated as a result of refining processes and maintenance operations. General guidance on the storage, handling, treatment, and disposal of hazardous and non-hazardous wastes is provided in the **General EHS Guidelines**.

Spent Catalysts

40. Spent catalysts result from several process units in petroleum refining, including the pretreating and catalytic reformer; light- and middle-distillate hydrodesulfurization; the hydrocracker; FCCU; RCCU; MTBE/ETBE and TAME production; butanes isomerization; the dienes hydrogenation and butylenes hydroisomerization unit; sulfuric acid regeneration; selective catalytic hydrodesulfurization; 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. There are several types of spent catalysts, and their physiochemical properties influence their handling. The two primary considerations are whether the specific catalyst is considered to be “hazardous” or “non-hazardous” in nature, and whether the metal(s) they contain are valuable or recoverable. An analysis of these factors will directly influence the handling of a spent catalyst.

41. Recommended management strategies for hazardous catalysts include the following:

- Use long-life catalysts and regeneration to extend the catalyst lifecycle;
- Use appropriate on-site storage and handling methods to avoid uncontrolled exothermic reactions; and
- 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 the **General EHS Guidelines**.

Other Hazardous Wastes

42. In addition to hazardous spent catalysts, industrial hazardous waste may include solvents; filters; mineral spirits; used sweetening; spent amines for CO₂, H₂S, and carbonyl sulfide (COS) removal; activated carbon filters and oily sludge from oil/water separators and desalters; tank emulsions or 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 HF alkylation, may be generated from crude oil storage tanks, desalting and topping, coking, propane, propylene, butanes streams dryers, and butanes isomerization. WWTPs and basins/lagoons generate sludge that may need to be considered as hazardous waste, depending on the treatment process itself and on the incoming wastewater.

43. 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**.

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

- Send oily sludges—such as those from crude oil storage tanks (bottom drains) and from desalter (bottom drains)—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 wastewater 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 or cement kilns, where feasible. In some cases, the residue may require stabilization prior to disposal to reduce the leachability of toxic metals. When not treated, the hazardous sludge from crude oil refineries must be disposed of in a secured landfill, as indicated in the **General EHS Guidelines**.

Non-Hazardous Wastes

45. HF alkylation produces neutralization sludge, 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 uses—in steel mills, for example—or landfilled. Detailed guidance on the storage, handling, treatment, and disposal of non-hazardous wastes is provided in the **General EHS Guidelines**.

Noise

46. 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), blowers, fans, and heaters. In addition, steam leaks, if significant, can be noisy. During emergency depressurization, high noise levels

can be generated due to high-pressure gases released 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

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

48. As a general approach, process health and safety management planning should include the adoption of a systematic and structured approach for the prevention and control of physical, chemical, biological, and radiological health and safety hazards described in the **General EHS Guidelines**.

49. Major occupational health and safety hazards should be prevented through the implementation of a Process Safety Management Program that includes all of the minimum elements outlined in the **General EHS Guidelines**, including:

- Facility-wide risk analysis, including a detailed consequence analysis (e.g., failure mode and effects analysis (FMEA), hazard identification study (HAZID), hazard and operability study (HAZOP), or quantitative risk assessment (QRA)). This analysis is expected to be carried out alongside the Front End Engineering Design (FEED) and with the Detailed Engineering Design prior to commissioning;
- Employee training on operational hazards;
- Procedures for the management of change in operations, process hazard analysis, maintenance of mechanical integrity, pre-start review, hot work permits, safe systems of work (SSW), and other essential aspects of process safety included in the **General EHS Guidelines**;
- 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, transportation, and storage of hazardous materials.

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

- Process safety;
- Oxygen-deficient atmosphere;
- Chemical hazards;
- Fire and explosions.

Process Safety

51. Process safety programs should be implemented based on industry-specific conditions, such as complex chemical reactions, use of hazardous materials (e.g., toxic, reactive, volatile, flammable, or explosive compounds), and multi-step reactions.

52. Process safety management should include the following:

- Physical hazard testing of materials and reactions;
- Hazard analysis studies to review the process chemistry and engineering practices, including thermodynamics and kinetics;
- Effective preventive maintenance routines and examination of the mechanical integrity of the process equipment and utilities;
- Operator/technician training and development; and
- Development of SSW, operating instructions, and emergency response procedures.

Oxygen-deficient Atmosphere

53. 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 the 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 sound an alarm warning of the uncontrolled release of nitrogen (including the presence of oxygen-deficient atmospheres in working areas⁹), automatically initiate forced ventilation, and shut down equipment to 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

54. Releases of hydrofluoric acid, carbon monoxide, methanol, and H₂S may present occupational exposure hazards. H₂S leakage may occur from amine regeneration in amine treatment units, and SRUs. CO leakage may occur from FCCU and RCCU and from the syngas production section of the Hydrogen Plant. CO/air mixtures are explosive and spontaneous; explosive re-ignition may occur. H₂S poses an immediate fire hazard when mixed with air.

55. Workers may be exposed to potential inhalation hazards (e.g., H₂S, CO, VOCs, 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.¹⁰

⁹ 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 the air.

¹⁰ 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

Hydrofluoric Acid

56. Workers may be exposed to hydrofluoric acid (HF) in the HF alkylation unit. Occupational safety measures include the following:¹¹

- Reducing HF volatility by adding suitable vapor pressure suppression additives;
- Minimizing HF hold-up volume (circuit inventory);
- Designing the plant layout to limit the extent of the plant area exposed to potential HF hazards, and to facilitate escape routes for workers;
- Clearly identifying HF hazardous areas, and indicating where PPE must be adopted;
- Implementing a worker decontamination procedure in a dedicated area;
- Implementing a safety distance buffer between the HF alkylation unit, other process units, and the refinery boundary;
- Use of scrubbing systems to neutralize and remove HF prior to flaring;
- Use of an HF neutralization basin for wastewater before it is discharged into the refinery's oily wastewater 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; and
- 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

57. 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 H₂S may ignite even in the absence of ignition sources at temperatures that are 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 the accumulation of vapors in storage tanks (e.g., sulfuric acid and bitumen).

58. Recommended measures to prevent and control fire and explosion risks from process operations include the following:¹²

(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.

¹¹ Recommendations for the handling of hydrofluoric acid are available in American Petroleum Institute (API), *Recommended Practice* (RP) 751, "Safe Operation of Hydrofluoric Acid Alkylation Units" (Third Edition, June 2007).

¹² Further recommendations for fire and explosion hazards are available in API, RP 2001, "Fire Protection in Refineries" (2012).

- Designing, constructing, and operating petroleum refineries according to international standards¹³ 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 the QRA, and through application of internationally recognized fire safety standards;¹⁴
- Providing early warning systems, 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/containing the areas that may be potentially affected by the accidental releases of flammable liquids 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; and
 - Designing the oily wastewater system to avoid the propagation of fire.

59. 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

60. 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**.

61. 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**.

¹³ An example of good practice includes the U.S. National Fire Protection Association (NFPA), Code 30: "Flammable and Combustible Liquids" (Quincy, MA: NFPA, 2003), available at <http://www.nfpa.org/>. Further guidance to minimize exposure to static electricity and lightning is available in API, RP, "Protection against Ignitions Arising out of Static, Lightning, and Stray Currents" (2003).

¹⁴ An example of further information on safe spacing is NFPA Code 30 (2003).

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

Major Hazards¹⁵

63. 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.¹⁶ Main measures for reduction of these risks are presented in Section 1.2. Emergency planning, to prevent major hazards to the community 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. Additional guidance is provided in the **General EHS Guidelines**.

¹⁵ A detailed description of health and safety issues and prevention/control strategies associated with petroleum refining, is available in 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.

¹⁶ Further recommendations for fire and explosion hazards are available in API, RP 2001, "Fire Protection in Refineries" (2012).

2. PERFORMANCE INDICATORS MONITORING

2.1 Environment

Emissions and Effluent Guidelines

64. Tables 1 and 2 present emission and effluent guidelines for the Petroleum Refining sector. Guideline values for process emissions (such as FCCU, SRU, and combustion units) and effluents in this sector are indicative of good international industry practice, as reflected in relevant standards of countries with recognized regulatory frameworks. The guideline values 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.

65. 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**. Larger power source emissions from turbines, boilers, and engines are addressed in the **EHS Guidelines for Thermal Power Plants**. Emissions from multi-fuel fired combustion units such as process heaters and boilers are addressed in Table 1, together with other process emissions. Guidance on ambient considerations based on the total load of emissions is provided in the **General EHS Guidelines**.

66. Effluent guidelines are applicable to 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 ^b | mg/Nm ³ | 300 100 for FCCU |
| SO _x ^c | mg/Nm ³ | 150 for SRU; 300 for FCCU 500 |
| Particulate Matter (PM10) ^d | mg/Nm ³ | 25 |
| Vanadium ^e | mg/Nm ³ | 5 |
| Nickel | mg/Nm ³ | 1 |
| H ₂ S ^e | mg/Nm ³ | 5 |

a. Dry gas at 3 percent O₂.
 b. NO_x means NO+NO₂ expressed in NO₂ equivalent. Guideline value from European Commission Joint Research Center (EC JRC), "Best Available Techniques Reference (BREF) Document for the Refining of Mineral Oil and Gas" (2015).
 c. SO_x means SO₂ + SO₃ expressed in SO₂ equivalent.
 d. Guideline value from EC JRC, "BREF Document for the Refining of Mineral Oil and Gas" (2015). Particulate matter guideline value is also valid for FCCU.
 e. From G.S.R. 186(E) and 820(E), India Ministry of Environment and Forests Notification http://envfor.nic.in/legis/env_stand.htm.

Table 2. Liquid Effluents Levels for Petroleum Refining Facilities ^a

| Pollutant | Units | Guideline Value |
|------------------------------|-------|--------------------|
| pH | S.U. | 6 – 9 |
| BOD5 | mg/L | 30 ^b |
| COD | mg/L | 125 ^c |
| Total Suspended Solids (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 Free | mg/L | 1 0.1 |
| Lead | mg/L | 0.1 |
| Nickel | mg/L | 0.5 |
| Mercury | mg/L | 0.003 ^d |
| Arsenic | mg/L | 0.1 |
| Vanadium | mg/L | 1 |
| Phenol | mg/L | 0.2 |
| Benzene | mg/L | 0.05 ^e |
| Benzo(a)pyrene | mg/L | 0.05 |
| Sulfides | mg/L | 0.2 |
| Total Nitrogen | mg/L | 10 ^f |
| Total Phosphorus | mg/L | 2 |
| Temperature increase | °C | <3 ^g |

Notes:

- a. Assumes an integrated petroleum refining facility.
- b. Guideline value from EC JRC, BREF (2015) Table 3.16; National legislations may have lower values such as China: 20 mg/L.
- c. Guideline value from EC JRC, BREF (2015); National legislations may have lower values such as China: 120 mg/L.
- d. EC JRC, BREF (2015) Table 3.16.
- e. Guideline value from EC JRC, BREF (2015).
- f. The effluent concentration of nitrogen (total) may be up to 40 mg/l in processes that include hydrogenation.
- g. At the edge of a scientifically established mixing zone, which takes into account ambient water quality, receiving water use, potential receptors, and assimilative capacity.
EC JRC, BREF (2015) Table 3.16.

Environmental Monitoring

67. Environmental monitoring programs for the Petroleum Refining sector should be implemented to address all activities that have been identified to have potentially significant impacts on the environment, during both normal operations and upset conditions (emergencies and consequent flaring). Environmental

monitoring activities should be based on direct or indirect indicators of emissions, wastewater, and resource use applicable to the particular project, and for point sources of emissions this should include both concentration and mass flow rate of pollutants.

68. Monitoring frequency should be sufficient to provide representative data for the parameter being monitored. Monitoring should be conducted by trained individuals following suitable and appropriate monitoring and record-keeping procedures and using regularly calibrated and suitably 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**.

69. In order to improve the management of fugitive emissions from the entire petroleum refinery and to protect human health in affected communities, in addition to monitoring and management requirements described in Section 1.1 of this Guideline, fence line monitoring of benzene concentration should be done according to internationally recognized methodologies.¹⁷ Where annual average benzene concentrations associated with refinery emissions exceed the guideline value given in Table 3, corrective actions should be taken to reduce benzene emissions from refinery. Corrective actions and monitoring results should be reported.

| Table 3. Fence Line Monitoring Action Level | |
|--|----------------------------------|
| Pollutant | Guideline Value |
| Benzene | 9 µg/m ³ ^a |
| a. Annual average concentration that is corrected for background contribution. Guideline value from U.S. EPA 40CFR63 Subpart CC—National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries (2015). | |

Resource Use, Energy Consumption, Emission and Waste Generation

70. Tables 4 and 5 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 continuous improvement in these areas.

| Table 4. Resource and Energy Consumption | | | |
|---|---|---|--------------------|
| Parameter | Definition of Parameter | Unit | Industry Benchmark |
| Total Energy Consumption⁽¹⁾ | Total energy consumed by the process, including direct combustion, steam, electricity, etc. | MJ per metric ton of processed crude oil | 2,300–3,300 |
| Electric Power Consumption⁽¹⁾ | Total electricity consumed by the process | kWh per metric ton of processed crude oil | 22–31 |

¹⁷ Such as U.S. EPA, 40 CFR 63 Subpart CC- National Emission Standards for Hazardous Air Pollutants from Petroleum Refineries (2015).

| | | | |
|--|---|--|-----------|
| Fresh Make-up Water⁽²⁾ | The supply of raw filtered water that integrates drift and evaporation losses as well as blowdown | m ³ per metric ton of processed crude oil | 0.07–0.66 |
| Notes: | | | |
| 1. Based on CONCAWE, EU refinery energy systems and efficiency, Report No. 3/12. (2012); CONCAWE, Oil Refining Report No. 1/13 (2013); U.S. Energy Information Administration (EIA), Short Term Energy Outlook (2013). | | | |
| 2. Based on EC JRC, “BREF Document for the Refining of Mineral Oil and Gas” (2015). | | | |

| Table 5. Emission and Waste Generation | | |
|---|--|----------------------|
| Parameter | Unit | Industry Benchmark |
| Wastewater | m ³ /metric ton crude oil | 0.1–1.5 ¹ |
| Emissions | Metric ton /million metric tons of processed crude oil | 105,000–276,000 |
| CO ₂ ² | | 70–450 |
| NO _x ³ | | 60–150 |
| Particulate matter | | 60–300 |
| SO _x ⁴ | | 65–300 |
| Solid waste | | 10–100 |
| Notes: | | |
| 1. Based on European Commission Joint Research Center (EC JRC), “Best Available Techniques Reference (BREF) Document for the Refining of Mineral Oil and Gas” (2015). | | |
| 2. Not all GHGs, only total CO ₂ . Based on EC JRC, “BREF Document for the Refining of Mineral Oil and Gas” (2015). | | |
| 3. NO+NO ₂ expressed in NO ₂ equivalent. | | |
| 4. SO ₂ +SO ₃ expressed in SO ₂ equivalent. | | |

2.2 Occupational Health and Safety

Occupational Health and Safety Guidelines

71. 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 the American Conference of Governmental Industrial Hygienists (ACGIH),¹⁸ the Pocket Guide to Chemical Hazards published by the United States National Institute for Occupational Health and Safety (NIOSH),¹⁹ Permissible Exposure Limits (PELs) published by the Occupational Safety and Health Administration of the United States (OSHA),²⁰ and Indicative Occupational Exposure Limit Values published by European Union member states,²¹ or other similar sources.

¹⁸ Available at <http://www.acgih.org/store/>.

¹⁹ Available at <http://www.cdc.gov/niosh/npg/>.

²⁰ Available at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9992.

²¹ Available at <https://osha.europa.eu/en/legislation/directives/exposure-to-chemical-agents-and-chemical-safety/osh-related-aspects/council-directive-91-414-ec>.

Accident and Fatality Rates

72. Projects should endeavor to reduce the number of incidents and near misses among project workers (whether directly employed or subcontracted) to a rate of zero, especially incidents 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., U.S. Bureau of Labor Statistics and U.K. Health and Safety Executive).²²

Occupational Health and Safety Monitoring

73. The working environment should be monitored for occupational hazards relevant to the specific project. Monitoring should be designed and implemented by accredited professionals²³ 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.

²² Available at <http://www.bls.gov/iif/> and <http://www.hse.gov.uk/statistics/index.htm>.

²³ 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 PETROLEUM INDUSTRY ACTIVITIES

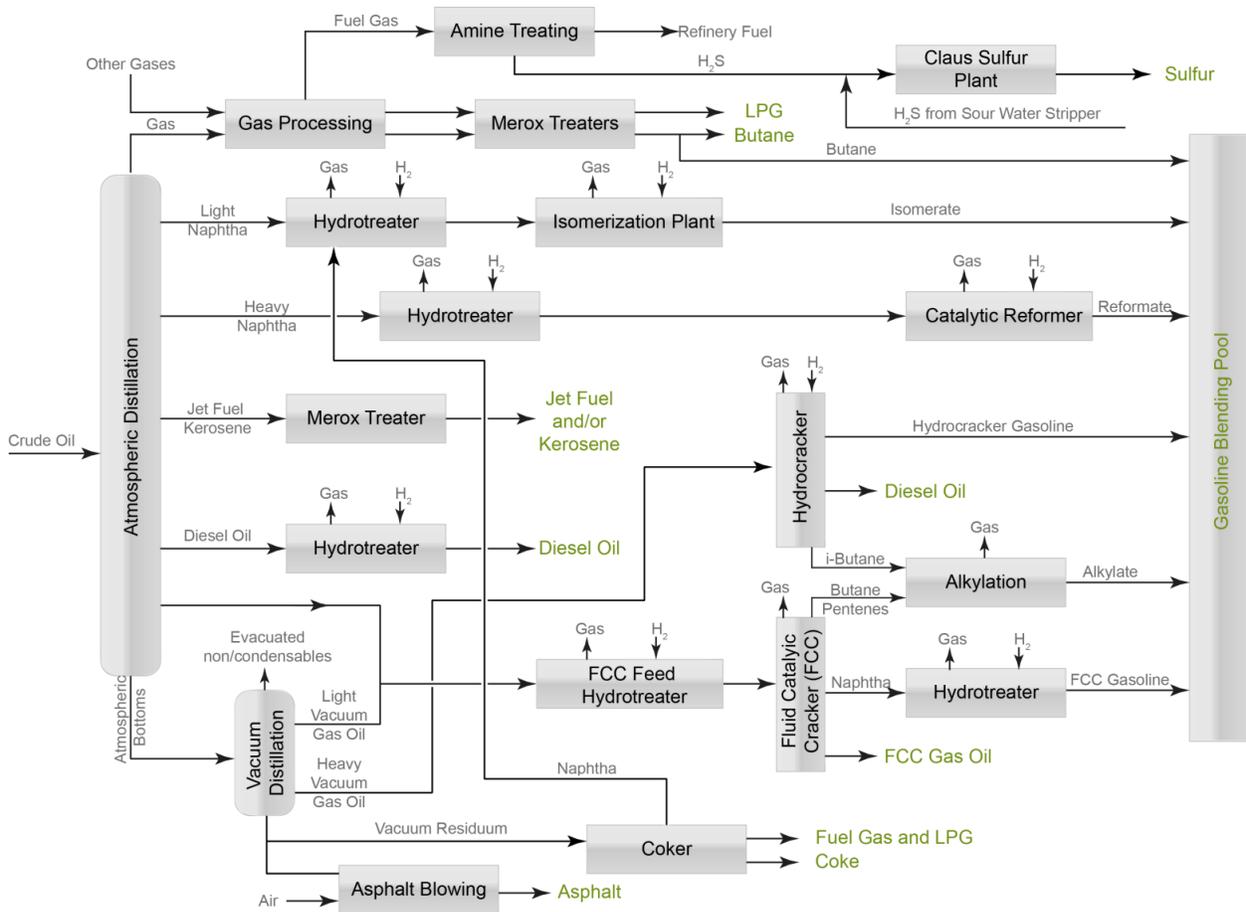
74. The **EHS Guidelines for Petroleum Refining** cover processing operations from crude oil to finished, refined, gaseous, liquid, and solid commercial products and by-products, including refinery fuel gas, liquefied petroleum gas (LPG), motor gasoline (Mo-Gas), kerosene diesel/gasoil, fuel oil, bitumen, asphalt, lubricant oils, waxes, sulfur, pet-coke, and intermediate products for the petrochemical industry (e.g., propane/propylene mixtures, virgin naphtha, aromatics, middle distillates, and vacuum distillates). Finished commercial products are produced from the blending of different intermediate products. These blends are normally referred to as gasoline pool (including cracked naphtha, reformate, isomerate, alkylate, methyl tertiary butyl ether (MTBE), t-amylmethyl ether (TAME), or ethanol, butane, etc.) diesel oil pool, and LPG pool, among others, and have varying compositions, depending on the configuration of the refinery process.

75. Petroleum refineries are complex systems designed specifically to produce the desired products based on 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. Modern refineries incorporate different processing units, capable of either high-conversion percentages (coking refineries), medium-conversion (cracking refineries), or low-conversion (hydro-skimming refineries), and are able to process different types of crude oil feed stocks (light, medium, heavy, paraffinic, aromatic, naphthenic (or cyclo-paraffinic)) with differing sulfur content, as in high density, high viscosity, high pour point, etc. An indication of a refinery's complexity can be assessed with the Nelson Complexity Index (NCI); for instance, an oil refinery with a high NCI ($6 < \text{NCI} < 9$), representing the secondary conversion capacity relative to the primary distillation capacity, is capable of producing high-quality refined products (i.e., Euro 5-grade gasoline), even when fed with heavy and sour crudes.

76. The refinery feedstock is crude oil, which is a mixture of hydrocarbon compounds.²⁴ The hydrocarbons in crude oil are a mixture of three chemical groups, including paraffins (normal and iso-paraffins), naphthenes (or cyclo-paraffins), and aromatics. The most common distinction between crude oil types is "sweet" and "sour." Sweet crude oil is normally low in sulfur content and lightly paraffinic. Sour crude oil is usually high in sulfur (more than 0.5 percent by weight) and heavily naphthenic. Crude oils are also classified into light, medium, and heavy, dependent on their content of paraffins, naphthenics, and aromatics.

²⁴ 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

77. Desalting is a process that involves washing the crude oil with fresh, brackish, or even sea water at a high temperature, using pressure to dissolve, separate, and remove the salts, water, and solids originally included in the raw crude. The washing water—generally pumped in counter-current through one or more desalting stages—displaces the equilibrium of salts (electrolytic components, as water), from the crude feed stream to the aqueous phase, namely the washing water, aided by carefully modulated electrostatic fields. Crude oil and/or reduced crude (commonly referred to as oily feedstock) and washing water are the input streams to the desalting unit, and washed, dehydrated, and desalted crude oil—as the contaminated oiled water—are its output streams. The salts containing some of the metals that can poison catalysts are dissolved in the water phase. After the oil has been washed and mixed as an emulsion of oil and water, demulsifying chemicals are then added and electrostatic fields are used to break the emulsion.

Primary Distillation Units

78. These units include the Atmospheric Distillation Unit (Topping or Crude Distillation Unit (CDU)), followed by the Vacuum Distillation Unit (VDU). 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 the bottom of the CDU (atmospheric residue) do not vaporize under the tower atmospheric pressure, and require further fractionation under vacuum conditions in the vacuum distillation tower; otherwise they would be subject to thermal degradation, due to extremely high boiling temperatures, if submitted to atmospheric distillation. The major benefits of VDU are the increased recovery of quantities of distillates (vacuum gas oils, vacuum distillates, and waxes) from the heavy residue of the atmospheric distillation.

Asphalt/Bitumen Production Unit

79. The Asphalt/Bitumen Production Unit is fed with vacuum residue. In the Bitumen Blowing Unit (BBU), also called the Asphalt/Bitumen Oxidation Unit, air is blown into the hot asphalt/bitumen, which causes dehydrogenation and polymerization reactions. This creates a harder product with increased viscosity, a higher softening point, and reduced penetration, making the asphalt/bitumen suitable for a range of applications, such as paving for roads. The blown asphalt/bitumen is removed from the bottom of the oxidation vessel and cooled before being sent to storage. Asphalt/bitumen is typically stored at 150–180°C in cone-roof tanks fitted with safety valves. These tanks are internally heated, insulated, and nitrogen blanketed. The nitrogen discharged to atmosphere may contain hydrocarbons and sulfur compounds in the form of aerosol-containing liquid droplets.

Hydrogen Consuming Processes

80. The products from the CDUs and the feeds to other units contain some natural impurities, such as sulfur, nitrogen, and other contaminants. Using the hydrotreating process, these impurities can be removed to reduce pollution when finished fuels (gasoline, diesel, fuel oils) are used and combusted. Hydrofinishing is used to modify other properties (i.e., aromatic content) as well. Heavy oils, high in sulfur and nitrogen, also require treatment prior to being fed to downstream catalytic conversion processes.

81. **Hydrotreating (Hydrodesulfurization & Hydrodenitrogenation)** are catalytic processes using hydrogen to perform a very mild hydrogenation of sulfur and nitrogen in hydrocarbons. In this process, sulfur and nitrogen are converted into hydrogen sulfide (H₂S) and ammonia (NH₃). The catalytic reaction (Cobalt (Co) and/or Nickel (Ni)-Mo catalysts) occurs from 370°C to 415°C; at higher temperatures, too much coke would form and catalyst life between regenerations would be too short. Naphtha, jet fuel, diesel, gas oil, lube oil, and fuel oil can all be treated in this way to remove deleterious substances.

82. Sulfur Hydrotreating²⁵ and hydro-processing processes, such as the Hydrodesulfurization of gasoil or naphtha, are used to remove impurities such as sulfur, nitrogen, oxygen, halides, and traces of metal impurities that may deactivate and even poison the noble metal catalysts, such as platinum, palladium, and

²⁵ 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), hydrodenitrification, saturation of olefins and saturation of aromatics, residue hydrotreating.

nickel. Hydrotreating also upgrades the quality of the processed fractions by converting olefins and diolefins into paraffins for the purpose of reducing gum (polyolefins) 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,²⁶ in which sulfur and nitrogen could have adverse effects on catalyst kinetics benefits. The global trend towards extracting heavy crudes from wells at the end of their lifecycles means that refineries require larger and larger hydrogen production plants to cope with the higher sulfur content (as a result of scraping the barrel). Against this background, more stringent regulations are being enforced concerning the maximum allowable H₂S (refined product) or sulfur dioxide (SO₂) (combustion flue gas) concentrations. 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 iso-paraffins, which have a much higher octane number. There are three distinct types of catalysts currently in use, including chloride-promoted catalysts, zeolites, and sulfated zirconium catalysts.

83. The dienes hydrogenation and butylenes hydroisomerization unit is placed upstream of the alkylation process and is 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 butene-2, which, in alkylation, leads to higher-octane gasoline components than those derived from butene-1.

Pretreating and Catalytic Reformer Unit

84. There are four major types of reactions that 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. The **Semi-Regenerative Catalytic Reformer (SRCR)** is typically comprised of three reactors, each with a fixed bed of catalyst. All of the catalyst is regenerated *in situ* during routine catalyst regeneration, which occurs approximately once every six to 24 months. The **Continuous Catalyst Regeneration Reformer (CCR)** is characterized by continuous *in-situ* regeneration of part of the catalyst in a special regenerator, and by continuous addition of the regenerated catalyst to the operating reactors. Coke deposits on the catalyst cause a decline in activity, with a reduction of octane number and reformate yield. The catalyst is regenerated by admitting hot air to remove the carbon from the catalyst, forming carbon monoxide (CO) and dioxide (CO₂), followed by chlorination. The high temperature required for regeneration causes the catalyst’s pores to collapse. Consequently, every two to three years the entire reformer must be shut down for catalyst change out. In the CCR, the major benefits may be summarized as follows: high conversion of olefins into paraffins, which are then reformed to a high-octane number value component for Mo-Gas blending, in conformity with the production of gasoline featuring the European Quality mark (EURO V). Other favorable benefits are a strong reduction of sulfur concentration from motor fuels, an increase in Research Octane Number (RON)

²⁶ 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.

of heavy naphtha and significant hydrogen resources for hydrotreating units, resulting from dehydrogenation reactions, typical of catalytic reforming.

Catalytic Cracking Units

85. Catalytic cracking is by far the most widely used conversion process to upgrade heavy hydrocarbons into the 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 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. The FCCU feed stream is the desulfurized heavy vacuum gasoil coming from hydrocracking. RCCU treats heavier feedstocks, such as the atmospheric distillation residue.

86. In both processes, oil and vapor come into contact with a hot catalyst in the “Riser Reactor.” The cracking process takes place in the 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. Current catalytic cracking processes are all fluidized bed processes (FCC) using powder catalysts (20–50 microns). Regeneration takes place continually, with some of the catalyst being sent from the reactor to the regenerator, and then from the regenerator to the reactor. Typical feedstocks of an FCC are; Vacuum Gas Oil, Atmospheric Gas Oil, Atmospheric Resid, Vacuum Resid, Coker Gas Oil, Visbreaker Gas Oil, and Deasphalted Oil. Typical products are gasoline, diesel oil, light fuel oils, and olefin-rich gases.

87. The FCCU is one of the major sources of air emissions within a refinery. Air emissions are associated mainly with the regenerator and are CO, CO₂, NO_x, particulates (mainly catalyst fines, including their constitutive heavy metals), and SO₂.

Gas Plant Units

88. 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 H₂S and carbonyl sulfide (COS) 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

89. The feedstocks of methyl tertiary butyl ether (**MTBE**)/ethyl tertiary butyl ether (**ETBE**) units are the C4 hydrocarbons stream coming from the FCCU, and methanol (CH₃OH) or ethanol (C₂H₅OH). Isobutylene reacts with CH₃O or C₂H₅O to yield directly MTBE or ETBE respectively. The reactors can be of the adiabatic or tubular type or combined with a fractionation tower (this type of reactor is normally referred to

as a Catalytic Distillation Reactor or Reactor Column). The catalyst is a sulfonic resin. The feedstock of TAME units is in light cracked naphtha (LCN), composed of C₅ hydrocarbons, both paraffins and olefins. However, only the reactive iso-amylenes (2-methyl-butene-1 and 2-methyl-butene-2) react with CH₄O to directly yield TAME. Adiabatic-type reactors are used, and the catalyst is the same as for the MTBE/ETBE units. Oxygenates, such as MTBE, ETBE, and TAME, were used originally simply as an additive to improve octane number. However, because of their oxygen content, they are now also added to reduce the CO and hydrocarbon in the emission gases.

Alkylation Units

90. The purpose of the alkylation unit is to produce a high-quality gasoline blending component called alkylate. Alkylation combines low-molecular-weight olefins (primarily a mixture of propylene and butylene) with iso-butane in the presence of a catalyst, either sulfuric acid or hydrofluoric acid (HF), to form higher-molecular-weight isoparaffins with a high-octane number (preferably iso-octane). The product (alkylate) is composed of a mixture of high-octane, branched-chain paraffinic hydrocarbons. Alkylate is a premium blending stock (RON up to 98). The octane number of alkylate depends on the type of olefins used, as well as on operating conditions.

91. The process involves low-temperature reaction conditions conducted in the presence of very strong acids (HF or non-fuming sulfuric acid). The reaction in HF alkylation produces acid-soluble oil (normally referred to 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) in a furnace together with fuel gas, where, at 1,050°C, the decomposition of the sulfuric acid into SO₂ 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

92. Polymerization is the process by which monomer units are bonded by covalent bonds to generate giant molecules; a “substance containing high-molecular-weight molecules, consisting of repeating units which are bonded to each other.”

93. In the polymerization process unit, the C₃ and C₄ olefins are dimerized and oligomerized to produce the so-called polymeric gasoline as a 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

94. 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. Basically, the coking units convert low-value residual fractions to lighter products of higher commercial value (wet gas, light and heavy gas oil) and petroleum coke. 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, H₂S and NH₃, 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.

95. **Cokers** have two, four, or eight coke drums; coking heater charge is delivered to one drum while the other drum/s are sequentially steam-stripped, water-cooled, and decoked. Steam is usually introduced in the heater tubes to control velocities and thus minimize coke deposition. The chemical reactions of delayed coking are complex, however three distinct reactions occur: partial vaporization and mild cracking (visbreaking) of the feed as it passes through the coker's furnace; cracking of the vapor occurs as it passes through the coke drum; and successive cracking and polymerization of the liquid trapped in the coke drum occurs until it is converted into vapor and coke.

96. In coke removal, when the coke drum in service is filled, it is isolated for safety reasons, steamed to remove hydrocarbon vapors, cooled by filling with water, opened, drained, and the coke removed. Most industrial plants use a hydraulic system for the decoking operation: high-pressure water jets, which are lowered into the coke bed on a rotating drill stem. The coke, which falls from the drum, is collected directly in railroad cars or pumped as liquid slurry to a stockpile. Then, in order to eliminate all volatile matter, it must be calcinated at about 1,100–1,250°C; this operation does not reduce the sulfur content. The sulfur contained in the coke is converted in flexicoking gasifiers, primarily into H₂S, and into traces of carbonyl sulfide (COS). The nitrogen contained in the coke is converted into NH₃.

Visbreaking Unit

97. The Visbreaking Unit is a well-established non-catalytic thermal cracking process that converts atmospheric or vacuum residues into gas, naphtha, distillates, and tar. It uses heat and pressure to break large hydrocarbon molecules into smaller, lighter molecules. The major benefits are process flexibility, allowing for direct processing of heavy oil residues, relative simplicity of the technology, and low capital and operating costs. Visbreaking is characterized by low conversion of petroleum residues, but allows for more than 10 times the reduction of viscosity, with the additional benefit of producing a standard fuel oil, making it possible to free most of the straight-run vacuum gasoil.

98. 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 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. However, excessive cracking leads to an unstable fuel oil, resulting in sludge and sediment formation during storage.

99. 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 H₂S.

Lube Oil Production Units

100. 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 (SRUs)

101. Sulfur is removed from a number of refinery process off-gas streams (sour gas) in order to meet the sulfur oxides (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 H₂S and COS, mixed with light refinery fuel gases. Before elemental sulfur is recovered, the fuel gases (primarily CH₄ and ethane) need to be separated from H₂S and COS. This is typically accomplished by dissolving H₂S and COS in a chemical solvent. The solvents most commonly used are amines, such as Monoethanolamine (MEA), diethanolamine (DEA), or mono-di-ethanolamine (MDEA). Dry adsorbent, such as molecular sieves, activated carbon, and iron sponge are also used.

102. In the amine solvent processes conducted in the amine gas treating units, a DEA solution (or other weak amine solution) is pumped to an absorption tower top section where the up-flowing acid gases are contacted in counter-current: H₂S and COS are dissolved in the solution, as well as carbon dioxide, if present. The fuel gases, free from H₂S and COS, are removed as treated, sweetened gaseous streams and sent to the refinery fuel gas network. The amine-H₂S and COS solution is regenerated by heating and steam-stripping to remove the H₂S gas before recycling back to the absorber. H₂S and COS are sent to the Claus Unit for sulfur recovery. Emissions to atmosphere from the sulfur recovery units (SRUs) will consist of H₂S, SO_x, and NO_x in the process tail gas, as well as fugitive emissions.

103. The Claus process consists of the partial combustion of the H₂S and COS-rich gas stream and then of reacting the resulting SO₂ and unburned H₂S in the presence of an aluminum oxide catalyst to produce elemental sulfur. Claus process sulfur recovery efficiency is in the range of 90 percent (one catalytic reactor) to 98 percent (three catalytic reactors). Tail Gas Treatment Units (TGTU) allow a further sulfur recovery (total SRU sulfur recovery efficiency up to 99 percent and over).

104. Air emissions from the SRU typically contain H₂S, SO_x, and NO_x. The SRU may also generate process wastewater that contains H₂S, NH₃, and the amines and residual wastes of spent catalysts.

Sour Water Stripper (SWSU)

105. Many process units generate sulfides and NH₃-contaminated water, normally referred to as sour water. The Sour Water Stripper Unit (SWSU) allows for the reuse of sour water by removing sulfides and NH₃. The process operation is complicated by the presence of other chemicals, such as phenol, and cyanides. SWSU treats sour water from the process unit and removes sour gases. Sour water stripping can be performed through different technologies. In one-stage stripping, the sour water is counter-currently stripped in a column by injected steam to remove H₂S and NH₃. In two-stage stripping, a first stage at low pH (6) improves H₂S removal, while the second stage at high pH (10) improves NH₃ removal. **Benefits:** Treated water can be re-used as desalter wash water. A two-stage SWS process can reach an overall H₂S and NH₃ recovery of 98 percent and 95 percent, respectively, associated with a residual concentration of 0.1–10 mg/l and 1–10 mg/l. Generated NH₃ can be used within the refinery.

Hydrogen Plant

106. Normally, the feedstock of the hydrogen plant is the methane obtained by the refinery process units, LPG, or refinery external natural gas, if available, but hydrodesulfurised naphtha can also be used as steam reformer feedstock. This unit normally consists of a **steam reformer** (top- or side-fired furnace), where the vaporized hydrocarbons feed steam through the tubes containing the catalyst. In its reaction with the steam, generally at about 40 bar, the catalyst produces a hydrogen–CO mixture referred to as synthetic gas (syngas). After passing through an important heat-recovery section, cold syngas enters the shift conversion reactor where, under an iron- or copper-based catalyst, CO 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 wastewater treatment unit (WWTU). Most Hydrogen Generation Units (HGU) include also the **Pressure Swing Absorption (PSA)** section, where the purified hydrogen increases in concentration, due to the molecular sieve, retaining higher molecular weight components such as nitrogen, etc.

Chemical Treatment Units

107. Chemical treatments are used to achieve certain product specifications. The Extraction Sweetening Units are designed to reduce the mercaptan content of hydrocarbon streams to mitigate odor nuisance and to reduce corrosivity. These treatments are accomplished by either extraction or oxidation (such as with **MEROX**, already used in old-fashioned hydroskimming oil refineries) 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.

108. The spent caustic scrubbing liquor (spent caustic) coming from the extraction sweetening unit is one of the most problematic waste streams generated in refineries. This is primarily due to the very high sulfide concentration, which makes it unsuitable for direct discharge into WWTUs. High levels of sulfides can also create odor and safety problems when released as a gas.

109. 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 bio-treatment in the WWTU.

Gasification Units

110. 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 H₂S and COS, and the gas is treated in an amine treating unit.

Blending Facilities

111. 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 (using dedicated

software, based on a statistic database of major gasoline parameters, easy and quick to measure online and use for the suitable proportioning of blending) or in batch-blending tanks, using intermediate run-down tanks.

112. Emissions to atmosphere from blending include fugitive VOCs from blending tanks, valves, pumps, and mixing operations.

Auxiliary Facilities

113. Auxiliary facilities at petroleum refineries typically consist of WWTUs, blowdown 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, and gas turbines).

114. Vapor Flare Systems: The main functions of flare systems are:

- The disposal of gas during normal operations;
- The disposal of gas during gas processing trips;
- To prepare for the repair/maintenance of process equipment;
- Emergencies; and
- Avoidance of venting.