

# Petroleum Refining

## Industry Description and Practices

The petroleum industry is organized into four broad sectors: exploration and production of crude oil and natural gas; transport; refining; and marketing and distribution. This document addresses only petroleum refining.

Crude oil is fractionated into liquefied petroleum gas, naphtha (used to produce gasoline by blending with octane boosters), kerosene/aviation turbine fuel, diesel oil, and residual fuel oil. Catalytic cracking and reforming, thermal cracking, and other secondary processes are used to achieve the desired product specifications. Certain refineries also produce feedstocks for the manufacture of lubricating oils and bitumens. Some refineries also manufacture coke.

## Waste Characteristics

Boilers, process heaters, and other process equipment are responsible for the emission of particulates, carbon monoxide, nitrogen oxides (NO<sub>x</sub>), sulfur oxides (SO<sub>x</sub>), and carbon dioxide. Catalyst changeovers and cokers release particulates. Volatile organic compounds (VOCs) such as benzene, toluene, and xylene are released from storage, product loading and handling facilities, and oil-water separation systems and as fugitive emissions from flanges, valves, seals, and drains. For each ton of crude processed, emissions from refineries may be approximately as follows:

- Particulate matter: 0.8 kilograms (kg), ranging from less than 0.1 to 3 kg.
- Sulfur oxides: 1.3 kg, ranging 0.2–0.6 kg; 0.1 kg with the Claus sulfur recovery process.
- Nitrogen oxides: 0.3 kg, ranging 0.06–0.5 kg.

- Benzene, toluene, and xylene (BTX): 2.5 grams (g), ranging 0.75 to 6 g; 1 g with the Claus sulfur recovery process. Of this, about 0.14 g benzene, 0.55 g toluene, and 1.8 g xylene may be released per ton of crude processed.
- VOC emissions depend on the production techniques, emissions control techniques, equipment maintenance, and climate conditions and may be 1 kg per ton of crude processed (ranging from 0.5 to 6 kg/t of crude).

Petroleum refineries use relatively large volumes of water, especially for cooling systems. Surface water runoff and sanitary wastewaters are also generated. The quantity of wastewaters generated and their characteristics depend on the process configuration. As a general guide, approximately 3.5–5 cubic meters (m<sup>3</sup>) of wastewater per ton of crude are generated when cooling water is recycled. Refineries generate polluted wastewaters, containing biochemical oxygen demand (BOD) and chemical oxygen demand (COD) levels of approximately 150–250 milligrams per liter (mg/l) and 300–600 mg/l, respectively; phenol levels of 20–200 mg/l; oil levels of 100–300 mg/l in desalter water and up to 5,000 mg/l in tank bottoms; benzene levels of 1–100 mg/l; benzo(a)pyrene levels of less than 1 to 100 mg/l; heavy metals levels of 0.1–100 mg/l for chrome and 0.2–10 mg/l for lead; and other pollutants. Refineries also generate solid wastes and sludges (ranging from 3 to 5 kg per ton of crude processed), 80% of which may be considered hazardous because of the presence of toxic organics and heavy metals.

*Accidental discharges of large quantities of pollutants can occur as a result of abnormal operation in a refinery and potentially pose a major local environmental hazard.*

## Pollution Prevention and Control

Petroleum refineries are complex plants, and the combination and sequence of processes is usually very specific to the characteristics of the raw materials (crude oil) and the products. Specific pollution prevention or source reduction measures can often be determined only by the technical staff. However, there are a number of broad areas where improvements are often possible, and site-specific waste reduction measures in these areas should be designed into the plant and targeted by management of operating plants. Areas where efforts should be concentrated are discussed here.

### *Reduction of Air Emissions*

- Minimize losses from storage tanks and product transfer areas by methods such as vapor recovery systems and double seals.
- Minimize SO<sub>x</sub> emissions either through desulfurization of fuels, to the extent feasible, or by directing the use of high-sulfur fuels to units equipped with SO<sub>x</sub> emissions controls.
- Recover sulfur from tail gases in high-efficiency sulfur recovery units.
- Recover non-silica-based (i.e., metallic) catalysts and reduce particulate emissions.
- Use low-NO<sub>x</sub> burners to reduce nitrogen oxide emissions.
- Avoid and limit fugitive emissions by proper process design and maintenance.
- Keep fuel usage to a minimum.

### *Elimination or Reduction of Pollutants*

- Consider reformat and other octane boosters instead of tetraethyl lead and other organic lead compounds for octane boosting.
- Use non-chrome-based inhibitors in cooling water, where inhibitors are needed.
- Use long-life catalysts and regenerate to extend the catalysts' life cycle.

### *Recycling and Reuse*

- Recycle cooling water and, where cost-effective, treated wastewater.

- Maximize recovery of oil from oily wastewaters and sludges. Minimize losses of oil to the effluent system.
- Recover and reuse phenols, caustics, and solvents from their spent solutions.
- Return oily sludges to coking units or crude distillation units.

### *Operating Procedures*

- Segregate oily wastewaters from stormwater systems.
- Reduce oil losses during tank drainage carried out to remove water before product dispatch.
- Optimize frequency of tank and equipment cleaning to avoid accumulating residue at the bottom of the tanks.
- Prevent solids and oily wastes from entering the drainage system.
- Institute dry sweeping instead of washdown to reduce wastewater volumes.
- Establish and maintain an emergency preparedness and response plan and carry out frequent training.
- Practice corrosion monitoring, prevention, and control in underground piping and tank bottoms.
- Establish leak detection and repair programs.

### **Target Pollution Loads**

Implementation of pollution prevention measures can yield both economic and environmental benefits. However, a balance on energy usage and environmental impacts may have to be struck. The production-related targets described below can be achieved by measures such as those detailed in the previous section. The values relate to the production processes before the addition of pollution control measures.

New refineries should be designed to maximize energy conservation and reduce hydrocarbon losses. A good practice target for simple refineries (i.e., refineries with distillation, catalytic reforming, hydrotreating, and offsite facilities) is that the total quantity of oil consumed as fuel and lost in production operations should not exceed 3.5% of the throughput. For refineries with secondary conversion units (i.e., hydrocrackers

or lubricating oil units), the target should be 5–6% (and, in some cases, up to 10%) of the throughput. Fugitive VOC emissions from the process units can be reduced to 0.05% of the throughput, with total VOC emissions of less than 1 kg per ton of crude (or 0.1% of throughput). Methods of estimating these figures include emissions monitoring, mass balance, and inventories of emissions sources. Design assumptions should be recorded to allow for subsequent computation and reduction of losses.

Vapor recovery systems to control losses of VOCs from storage tanks and loading areas should achieve 90–100% recovery.

Plant operators should aim at using fuel with less than 0.5% sulfur (or an emissions level corresponding to 0.5% sulfur in fuel). High-sulfur fuels should be directed to units equipped with SO<sub>x</sub> controls. Fuel blending is another option. A sulfur recovery system that achieves at least 97% (but preferably over 99%) sulfur recovery should be used when the hydrogen sulfide concentration in tail gases exceeds 230 mg/Nm<sup>3</sup>. The total release of sulfur dioxide should be below 0.5 kg per ton for a hydroskimming refinery and below 1 kg per ton for a conversion refinery.

A wastewater generation rate of 0.4 m<sup>3</sup>/t of crude processed is achievable with good design and operation, and new refineries should achieve this target as a minimum.

The generation rate of solid wastes and sludges should be less than 0.5% of the crude processed, with a target of 0.3%.

## Treatment Technologies

### *Air Emissions*

Control of air emissions normally includes the capture and recycling or combustion of emissions from vents, product transfer points, storage tanks, and other handling equipment. Boilers, heaters, other combustion devices, cokers, and catalytic units may require particulate matter controls. Use of a carbon monoxide boiler is normally a standard practice in the fluidized catalytic cracking units. Catalytic cracking units should be provided with particular removal devices. Steam injection in flaring stacks can reduce particulate matter emissions.

### *Liquid Effluents*

Refinery wastewaters often require a combination of treatment methods to remove oil and contaminants before discharge. Separation of different streams, such as stormwater, cooling water, process water, sanitary, sewage, etc., is essential for minimizing treatment requirements. A typical system may include sour water stripper, gravity separation of oil and water, dissolved air flotation, biological treatment, and clarification. A final polishing step using filtration, activated carbon, or chemical treatment may also be required. Achievable pollutant loads per ton of crude processed include BOD, 6 g; COD, 50 g; suspended solids, 10 g; and oil and grease, 2 g.

### *Solid and Hazardous Wastes*

Sludge treatment is usually performed using land application (bioremediation) or solvent extraction followed by combustion of the residue or by use for asphalt, where feasible. In some cases, the residue may require stabilization prior to disposal to reduce the leachability of toxic metals.

Oil is recovered from slops using separation techniques such as gravity separators and centrifuges.

## Emissions Guidelines

Emissions levels for the design and operation of each project must be established through the environmental assessment (EA) process on the basis of country legislation and the *Pollution Prevention and Abatement Handbook*, as applied to local conditions. The emissions levels selected must be justified in the EA and acceptable to the World Bank Group.

The guidelines given below present emissions levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance. Any deviations from these levels must be described in the World Bank Group project documentation. The emissions levels given here can be consistently achieved by well-designed, well-operated, and well-maintained pollution control systems.

The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions

or effluents to achieve these guidelines is unacceptable.

All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

*Air Emissions*

The emissions levels presented in Table 1 should be achieved.

*Liquid Effluents*

The emissions levels presented in Table 2 should be achieved.

Effluent requirements are for direct discharge to surface waters. Discharge to an offsite wastewater treatment plant should meet applicable pretreatment requirements.

*Solid Wastes and Sludges*

Wherever possible, generation of sludges should be minimized to 0.3 kg per ton of crude processed, with a maximum of 0.5 kg per ton of crude processed. Sludges must be treated and stabilized to reduce concentrations of toxics (such as benzene and lead) in leachate to acceptable levels, for example, below 0.05 milligram per kg.

*Ambient Noise*

Noise abatement measures should achieve either the levels given below or a maximum increase in background levels of 3 decibels (measured on the

**Table 1. Emissions from the Petroleum Industry**  
(milligrams per normal cubic meter)

<i>Parameter</i>	<i>Maximum value</i>
PM	50
Nitrogen oxides <sup>a</sup>	460
Sulfur oxides	150 for sulfur recovery units; 500 for other units
Nickel and vanadium (combined)	2
Hydrogen sulfide	152

a. Excludes NO<sub>x</sub> emissions from catalytic units.

**Table 2. Effluents from the Petroleum Industry**  
(milligrams per liter)

<i>Parameter</i>	<i>Maximum value</i>
pH	6–9
BOD	30
COD	150
TSS	30
Oil and grease	10
Chromium	
Hexavalent	0.1
Total	0.5
Lead	0.1
Phenol	0.5
Benzene	0.05
Benzo(a)pyrene	0.05
Sulfide	1
Nitrogen (total) <sup>a</sup>	10
Temperature increase	≤ 3°C <sup>b</sup>

a. The maximum effluent concentration of nitrogen (total) may be up to 40 mg/l in processes that include hydrogenation.

b. The effluent should result in a temperature increase of no more than 3° C at the edge of the zone where initial mixing and dilution take place. Where the zone is not defined, use 100 meters from the point of discharge, provided there are no sensitive ecosystems within this range.

A scale) [dB(A)]. Measurements are to be taken at noise receptors located outside the project property boundary.

<i>Receptor</i>	<i>Maximum allowable log equivalent (hourly measurements), in dB(A)</i>	
	<i>Day</i>	<i>Night</i>
	<i>(07:00–22:00)</i>	<i>(22:00–07:00)</i>
Residential, institutional, educational	55	45
Industrial, commercial	70	70

**Monitoring and Reporting**

Frequent sampling may be required during start-up and upset conditions. Once a record of consistent performance has been established, sampling for the parameters listed in this document should be as described below.

Air emissions from stacks should be monitored once every shift, if not continuously, for opacity (maximum level, 10%). Air emissions of hydro-

gen sulfide from a sulfur recovery unit should be monitored on a continuous basis. Annual emissions monitoring of combustion sources should be carried out for sulfur oxides (sulfur content of the fuel monitored on a supply-tank basis) and for nitrogen oxides.

Liquid effluents should be monitored daily for all the parameters listed above, except that metals should be monitored at least monthly.

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. Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required.

### Key Issues

The key production and control practices that will lead to compliance with emissions guidelines can be summarized as follows:

- Use vapor recovery systems to reduce VOC emissions.
- Install sulfur recovery systems, where feasible.
- Use low-NO<sub>x</sub> burners.
- Maintain fuel and losses to 3.5% for simple refineries and below 6% (with 10% as the maximum) for refineries with secondary processing.
- Recover and recycle oily wastes.
- Regenerate and reuse spent catalysts and solvents.
- Recycle cooling water and minimize wastewaters.
- Segregate storm water from process wastewater.
- Use nonchrome-based inhibitors (use only to the extent needed in cooling water).
- Minimize the generation of sludges.
- Install spill prevention and control measures.

### Sources

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