Petrochemicals Manufacturing

Industry Description and Practices

Natural gas and crude distillates such as naphtha from petroleum refining are used as feedstocks to manufacture a wide variety of petrochemicals that are in turn used in the manufacture of consumer goods. The description of petrochemical processes and products presented here is for illustrative purposes only. The basic petrochemicals manufactured by cracking, reforming, and other processes include olefins (such as ethylene, propylene, butylenes, and butadiene) and aromatics (such as benzene, toluene, and xylenes). The capacity of naphtha crackers is generally of the order of 250,000–750,000 metric tons per year (tpy) of ethylene production. Some petrochemical plants also have alcohol and oxo-compound manufacturing units on site. The base petrochemicals or products derived from them, along with other raw materials, are converted to a wide range of products. Among them are:

- Resins and plastics such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polypropylene, polystyrene, and polyvinyl chloride (PVC)
- Synthetic fibers such as polyester and acrylic
- Engineering polymers such as acrylonitrile butadiene styrene (ABS)
- Rubbers, including styrene butadiene rubber (SBR) and polybutadiene rubber (PBR)
- Solvents
- Industrial chemicals, including those used for the manufacture of detergents such as linear alkyl benzene (LAB) and of coatings, dyestuffs, agrochemicals, pharmaceuticals, and explosives.

A number of alternative methods for manufacturing the desired products are available. Details on typical processes and products are provided in the Annex.

Waste Characteristics

Fugitive air emissions from pumps, valves, flanges, storage tanks, loading and unloading operations, and wastewater treatment are of greatest concern. Some of the compounds released to air are carcinogenic or toxic. Ethylene and propylene emissions are of concern because their release can lead to the formation of extremely toxic oxides. Compounds considered carcinogenic that may be present in air emissions include benzene, butadiene, 1,2-dichloroethane, and vinyl chloride. A typical naphtha cracker at a petrochemical complex may release annually about 2,500 metric tons of alkenes, such as propylenes and ethylene, in producing 500,000 metric tons of ethylene. Boilers, process heaters, flares, and other process equipment (which in some cases may include catalyst regenerators) are responsible for the emission of particulates, carbon monoxide, nitrogen oxides (200 tpy), based on 500,000 tpy of ethylene capacity, and sulfur oxides (600 tpy).

The release of volatile organic compounds (VOCs) into the air depends on the products handled at the plant. VOCs released may include acetaldehyde, acetone, benzene, toluene, trichloroethylene, trichlorotoluene, and xylene. VOC emissions are mostly fugitive and depend on the production processes, materials-handling and effluent-treatment procedures, equipment maintenance, and climatic conditions. VOC emissions from a naphtha cracker range from 0.6 to 10 kilograms per metric ton (kg/t) of ethylene produced. Of these emissions, 75% consists of alkanes, 20% of unsaturated hydrocarbons, about half of which is ethylene, and 5% of aromatics. For a vinyl chloride plant, VOC emissions are 0.02–2.5 kg/t of product; 45% is ethylene dichloride, 20% vinyl chloride, and 15% chlorinated organics; for an SBR plant, VOC emissions are 3–10 kg/t of product; for an ethyl benzene plant, 0.1-2 kg/t of product; for an ABS plant, 1.4–27 kg/t of product; for a styrene plant, 0.25–18 kg/t of product; and for a polystyrene plant, 0.2–5 kg/t of product. Petrochemical units generate wastewaters from process operations such as vapor condensation, from cooling tower blowdown, and from stormwater runoff. Process wastewaters are generated at a rate of about 15 cubic meters per hour (m^3/hr), based on 500,000 tpy ethylene production, and may contain biochemical oxygen demand (BOD) levels of 100 mg/l, as well as chemical oxygen demand (COD) of 1,500–6,000 mg/l, suspended solids of 100–400 mg/l, and oil and grease of 30–600 mg/l. Phenol levels of up to 200 mg/l and benzene levels of up to 100 mg/l may also be present.

Petrochemical plants generate solid wastes and sludges, some of which may be considered hazardous because of the presence of toxic organics and heavy metals. Spent caustic and other hazardous wastes may be generated in significant quantities; examples are distillation residues associated with units handling acetaldehyde, acetonitrile, benzyl chloride, carbon tetrachloride, cumene, phthallic anhydride, nitrobenzene, methyl ethyl pyridine, toluene diisocyanate, trichloroethane, trichloroethylene, perchloroethylene, aniline, chlorobenzenes, dimethyl hydrazine, ethylene dibromide, toluenediamine, epichlorohydrin, ethyl chloride, ethylene dichloride, and vinyl chloride.

Accidental discharges as a result of abnormal operation, especially from polyethylene and ethylene-oxide-glycol plants in a petrochemical complex, can be a major environmental hazard, releasing large quantities of pollutants and products into the environment. Plant safety and fire prevention and control procedures should be in place.

Pollution Prevention and Control

Petrochemical plants are typically large and complex, and the combination and sequence of processes are usually specific to the characteristics of the products manufactured. Specific pollution prevention or source reduction measures are best determined by technical staff. However, there are a number of broad areas where improvements are often possible, and site-specific emission reduction measures in these areas should be designed into the plant and targeted by plant management. Areas where efforts should be concentrated are discussed below.

Reduction of Air Emissions

- Minimize leakages of volatile organics, including benzene, vinyl chloride, and ethylene oxide, from valves, pump glands (through use of mechanical seals), flanges, and other process equipment by following good design practices and equipment maintenance procedures.
- Use mechanical seals where appropriate.
- Minimize losses from storage tanks, product transfer areas, and other process areas by adopting methods such as vapor recovery systems and double seals (for floating roof tanks).
- Recover catalysts and reduce particulate emissions.
- Reduce nitrogen oxide (NO_x) emissions by using low-NO_x burners. Optimize fuel usage.

In some cases, organics that cannot be recovered are effectively destroyed by routing them to flares and other combustion devices.

Elimination or Reduction of Pollutants

- Use nonchrome-based additives in cooling water.
- Use long-life catalysts and regeneration to extend the cycle.

Recycling and Reuse

- Recycle cooling water and treated wastewater to the extent feasible.
- Recover and reuse spent solvents and other chemicals to the extent feasible.

Improved Operating Procedures

- Segregate process wastewaters from stormwater systems.

- Optimize the frequency of tank and equipment cleaning.
- Prevent solids and oily wastes from entering the drainage system.
- Establish and maintain an emergency preparedness and response plan.

Target Pollution Loads

Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits. The following production-related targets can be achieved by measures such as those described in the previous section. The figures relate to the production processes before the addition of pollution control measures.

A good practice target for petrochemical complex is to reduce total organic emissions (including VOCs) from the process units to 0.6% of the throughput. Target maximum levels for air releases, per ton of product, are, for ethylene, 0.06 kg; for ethylene oxide, 0.02 kg; for vinyl chloride, 0.2 kg; and for 1,2-dichloroethane, 0.4 kg. Methods of estimating these figures include ambient and emissions monitoring, emission factors, 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 close to 100% recovery.

A wastewater generation rate of 15 cubic meters per 100 tons of ethylene produced is achievable with good design and operation; and new petrochemical complexes should strive to achieve this.

Treatment Technologies

Air Emissions

Control of air emissions normally includes the capturing and recycling or combustion of emissions from vents, product transfer points, storage tanks, and other handling equipment.

Catalytic cracking units should be provided with particulate removal devices. Particulate removal technologies include fabric filters, ceramic filters, wet scrubbers, and electrostatic precipitators. Gaseous releases are minimized by condensation, absorption, adsorption (using activated carbon, silica gel, activated alumina, and zeolites), and, in some cases, biofiltration and bioscrubbing (using peat or heather, bark, composts, and bioflora to treat biodegradable organics), and thermal decomposition.

Liquid Effluents

Petrochemical wastewaters often require a combination of treatment methods to remove oil and other contaminants before discharge. Separation of different streams (such as stormwater) is essential to minimize treatment requirements. Oil is recovered using separation techniques. For heavy metals, a combination of oxidation / reduction, precipitation, and filtration is used. For organics, a combination of air or steam stripping, granular activated carbon, wet oxidation, ion exchange, reverse osmosis, and electrodialysis is used. A typical system may include neutralization, coagulation / flocculation, flotation / sedimentation / filtration, biodegradation (trickling filter, anaerobic, aerated lagoon, rotating biological contactor, and activated sludge), and clarification. A final polishing step using filtration, ozonation, activated carbon, or chemical treatment may also be required. Examples of pollutant loads that can be achieved are: COD, less than 1 kg per 100 tons of ethylene produced; suspended solids, less than 0.4 kg / 100 t; and dichloroethane, than 0.001 kg / 100 t.

Solid and Hazardous Wastes

Combustion (preceded in some cases by solvent extraction) of toxic organics is considered an effective treatment technology for petrochemical organic wastes. Steam stripping and oxidation are also used for treating organic waste streams. Spent catalysts are generally sent back to the suppliers. In some cases, the solid wastes may require stabilization to reduce the leachability of toxic metals before disposal of in an approved, secure landfill.

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 effluent levels presented in Table 2 should be achieved.

Table 1, Emissions from Petrochemicals Manufacturing and Target Ambient Levels

(miligrams per normal cubic meter)

Parameter	*Maximum value*
PM	20
Nitrogen oxides	300
Hydrogen chloride	10
Sulfur oxides	500
Benzene	5 mg/m^3 for emissions; 0.1 ppb at the plant fence
1,2-dichloroethane	5 mg/m^3 for emissions; 1.0 ppb at the plant fence
Vinyl chloride	5 mg/m^3 for emissions; 0.4 ppb at the plant fence
Ammonia	15 mg/m^3

Note: Maximum ambient levels for ethylene oxide are 0.3 parts per billion (ppb) at the plant fence. Maximum total emissions of the VOCs acetaldehyde, acrylic acid, benzyl chloride, carbon tetrachloride, chlorofluorocarbons, ethyl acrylate, halons, maleic anhydride, 1, 1, 1 trichlorethane, trichloroethylene, and trichlorotoluene are 20 mg/Nm^3. Maximum total heavy metals emissions are 1.5 mg/Nm^3.

Table 2. Effluents from Petrochemicals Manufacturing

(milligrams per liter, except for pH and temperature)

Parameter	*Maximum value*
pH	6–9
BOD	30
COD	150
TSS	30
Oil and grease	10
Cadmium	0.1
Chromium (hexavalent)	0.1
Copper	0.5
Phenol	0.5
Benzene	0.05
Vinyl chloride	0.05
Sulfide	1
Nitrogen (total)	10
Temperature increase	≤ 3°C[a]

Note: Effluent requirements are for direct discharge to surface waters.

a. 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.

Solid Wastes and Sludges

Wherever possible, generation of sludges should be minimized. Sludges must be treated to reduce toxic organics to nondetectable levels. Wastes containing toxic metals should be stabilized before disposal.

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

	Maximum allowable log equivalent (hourly measurements), in dB(A)	
Receptor	*Day (07:00–22:00)*	*Night (22:00–07:00)*
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 visually monitored for opacity at least once every eight hours. Annual emissions monitoring of combustion sources should be carried out for sulfur oxides, nitrogen oxides, and the organics listed above, with fuel sulfur content and excess oxygen maintained at acceptable levels during normal operations. Leakages should be visually checked every eight hours and at least once a week using leak detection equipment.

Liquid effluents should be monitored at least once every eight hours for all the parameters cited above except metals, which should be monitored at least monthly.

Each shipment of solid waste going for disposal should be monitored for toxics.

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:

- Implement an equipment maintenance program that minimizes releases of volatile organics, including ethylene oxide, benzene, vinyl chloride, and 1,2-dichloroethane.
- Install vapor recovery systems to reduce VOC emissions.
- Use low-NO_x burners.
- Optimize fuel usage.
- Regenerate and reuse spent catalysts, solvents, and other solutions to the extent feasible.
- Recycle cooling water and reuse wastewaters.
- Segregate stormwater from process wastewater.
- Use nonchrome-based additives in cooling water.
- Design and practice emergency preparedness and prevention measures.

Annex. Typical Processes and Products in Petrochemical Manufacturing

C_1 compounds (with one carbon atom in their molecule) manufactured at petrochemical plants include methanol, formaldehyde, and halogenated hydrocarbons. Formaldehyde is used in the manufacture of plastic resins, including phenolic, urea, and melamine resins. Halogenated hydrocarbons are used in the manufacture of silicone, solvents, refrigerants, and degreasing agents.

Olefins (organics having at least one double bond for carbon atoms) are typically manufactured from the steam cracking of hydrocarbons such as naphtha. Major olefins manufactured include ethylene (C_2, since it has two carbon atoms), propylene (C_3), butadiene (C_4), and acetylene. The olefins manufactured are used in the manufacture of polyethylene, including low-density polyethylene (LDPE) and high-density polyethylene (HDPE), and for polystyrene, polyvinyl chloride, ethylene glycol (used along with dimethyl terphthalate, DMT, as feedstock to the polyester manufacturing process), ethanol amines (used as solvents), polyvinyl acetate (used in plastics), polyisoprene (used for synthetic rubber manufacture), polypropylene, acetone (used as a solvent and in cosmetics), isopropanol (used as a solvent and in pharmaceuticals manufacturing), acrylonitrile (used in the manufacture of acrylic fibers and nitrile rubber), propylene glycol (used in pharmaceuticals manufacturing), and polyurethane.

Butadiene is used in the manufacture of polybutadiene rubber (PBR) and styrene butadiene rubber (SBR). Other C_4 compounds manufactured include butanol, which is used in the manufacture of solvents such as methyl ethyl ketone.

The major aromatics (organics having at least one ring structure with six carbon atoms) manufactured include benzene, toluene, xylene, and naphthalene. Other aromatics manufactured include phenol, chlorobenzene, styrene, phthalic and maleic anhydride, nitrobenzene, and aniline. Benzene is generally recovered from cracker streams at petrochemical plants and is used for the manufacture of phenol, styrene, aniline, nitrobenzene, sulfonated detergents, pesticides such as hexachlorobenzene, cyclohexane (an important intermediate in synthetic fiber manufacture), and caprolactam, used in the manufacture of nylon. Benzene is also used as a solvent.

The main uses of toluene are as a solvent in paints, rubber, and plastic cements and as a feedstock in the manufacture of organic chemicals, explosives, detergents, and polyurethane foams. Xylenes (which exist as three isomers) are used in the manufacture of DMT, alkyd resins, and plasticizers. Naphthalene is mainly used in the manufacture of dyes, pharmaceuticals, insect repellents, and phthalic anhydride (used in the manufacture of alkyd resins, plasticizers, and polyester).

The largest user of phenol in the form of thermosetting resins is the plastics industry. Phenol is also used as a solvent and in the manufacture of intermediates for pesticides, pharmaceuticals, and dyestuffs. Styrene is used in the manufacture of synthetic rubber and polystyrene resins. Phthalic anhydride is used in the manufacture of DMT, alkyd resins, and plasticizers such as phthalates. Maleic anhydride is used in the manufacture of polyesters and, to some extent, for alkyd resins. Minor uses include the manufacture of malathion and soil conditioners. Nitrobenzene is used in the manufacture of aniline, benzidine, and dyestuffs and as a solvent in polishes. Aniline is used in the manufacture of dyes, including azo dyes, and rubber chemicals such as vulcanization accelerators and antioxidants.

Sources

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