Multilateral Investment Guarantee Agency

Environmental Guidelines for

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 which are in turn used for the manufacture of a variety 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 (including ethylene, propylene, butylenes, and butadiene) and aromatics (including benzene, toluene, and xylenes). The capacity of naphtha crackers is generally of the order of 250,000 to 750,000 metric tons per year (tpy) of ethylene production. Some petrochemical plants also have alcohol and oxo-compounds 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 including 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 (PBR)); solvents; industrial chemicals (including those used for the manufacture of detergents such as linear alkyl benzene (LAB), coatings, dyestuff, agrochemicals, pharmaceuticals, and explosives). A number of alternative methods are available to manufacture the desired products. (Further details of 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 of their fate processes which lead to the formation of oxides which are extremely toxic. 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 annually release about 2,500 emetric tons of alkenes (such as propylenes and ethylene), when producing 500,000 metric tons of ethylene. Boilers, process heaters, flares, and other process equipment (in some cases may include catalyst regenerators)are responsible for the emission of particulates, carbon monoxide, nitrogen oxides (200 metric tons per year), and sulfur oxides (SO_x) (600 metric tons per year based on a 500,000 metric tons per year of ethylene capacity).

The release of volatile organic compounds (VOCs) to air depends on the products handled at the plant and may include acetaldehyde, acetone, benzene, toluene, trichloroethylene, trichlorotoluene, and xylene. VOC emissions are mostly fugitive and depend upon the production processes, material handling and effluent treatment procedures, equipment maintenance, and climatic conditions. VOC emissions from a naphtha cracker range from 0.6 to 10 kilograms (kg) (75% are alkanes, 20% unsaturated hydrocarbons about half of these is ethylene, and remaining 5% are aromatics) per metric ton of ethylene; 0.02 to 2.5 kg (45% of these being ethylene dichloride, 20% being vinyl chloride, and 15% being chlorinated organics) per metric ton of product in a vinyl chloride plant; 3-10 kg per metric ton of product in a SBR plant; 0.1-2 kg per metric ton of product in ethyl benzene plant; 1.4-27 kg per metric ton of product in ABS plant; 0.25-18 kg per metric ton of product in a styrene plant; and 0.2-5 kg per metric ton of product in a polystyrene plant.

Petrochemical units generate wastewaters from process operations (such as vapor condensation), cooling tower blow down, and storm water run off. Process wastewaters are generated at a rate of about 15 cubic meters per hour (m^3/hr) (based on a 500,000 metric tons per year ethylene production) and may contain biochemical oxygen demand (BOD_5) (100 mg/L), COD (1,500-6,000 mg/L), suspended solids (100-400 mg/L), and oil and grease (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 also 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 such as 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 may be generated in significant quantities.

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, where the combination and sequence of processes is usually very 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 effort should be concentrated include:

Reduction of Air Emissions

- Minimize the leakages of volatile organics (including benzene, vinyl chloride, and ethylene oxide) from valves, pump glands (use 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.
- Use low NO_x burners to reduce NO_x emissions.
- Optimize fuel usage.
- In some case, organics that cannot be recovered, are effectively destroyed by routing them to flares and other combustion devices.

Elimination/Reduction of Pollutants

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

Recycling/Reuse

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

Improved Operating Procedures

- Segregate process wastewaters from stormwater systems.
- Optimize tank and equipment cleaning frequency.
- 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 provide both economic and environmental benefits. The following production-related targets can be achieved by measures such as those detailed 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 that the total organic emissions (including VOCs) from the process units be reduced to 0.6% of the throughput. Target maximum levels for air releases of ethylene, ethylene oxide, vinyl chloride, and 1,2-dichloroethane are 0.06 kg, 0.02 kg, 0.2 kg, and 0.4 kg per ton of product. 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 15 m^3 per 100 tons of ethylene produced is achievable with good design and operation and new petrochemicals 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 (activated carbon, silica gel, activated alumina, and zeolites), and in some cases using biofiltration and bioscrubbing (using peat/heather, bark, composts, and bioflora for treating 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. Pollutants loads which can be achieved include a COD level of less than 1 kg, suspended solids level of less than 0.4 kg, and dichloroethane level of less than 0.001 kg, per 100 tons of ethylene produced.

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 in an approved secure landfill.

Emission Guidelines

Emission levels for the design and operation of each project must be established through the Environmental Assessment (EA) process, based on country legislation and the *Pollution Prevention and Abatement Handbook* as applied to local conditions. The emission levels selected must be justified in the EA and acceptable to MIGA.

The following guidelines present emission levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance, including MIGA guarantees; any deviations from these levels must be described in the project documentation.

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 following emissions levels should be achieved:

Emissions from Petrochemicals Manufacturing and Target Ambient Levels[i1 2]

Parameter	*Maximum value milligrams per normal cubic meter(mg/Nm³)*
Particulate matter (PM)	20
Nitrogen oxide (NO_x)	300
Hydrogen chloride	10
Sulfur oxide (SO_x)	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

[1] Maximum ambient levels for ethylene oxide are 0.3 ppb at the plant fence.

[1] Maximum VOC emissions total of acetaldehyde, acrylic acid, benzyl chloride, carbon tetrachloride, chlorofluorocarbons, ethyl acrylate, halons, maleic anhydride, 1, 1, 1 trichlorethane, trichloroethylene, and trichlorotoluene) should be 20 mg/Nm^3. Total heavy metals should be 1.5 mg/Nm^3.

Liquid Effluents

The following effluent levels should be achieved:

Effluents from Petrochemicals Manufacturing

Parameter	*Maximum value milligrams per liter (mg/L)*
pH	6 – 9
BOD_5	30
COD	150
Total suspended solids	30
Oil and grease	10
Cadmium	0.1

Effluents from Petrochemicals Manufacturing (cont'd)

Chromium (hexavalent)	0.1
Copper	0.5
Phenol	0.5
Benzene	0.05
Vinyl chloride	0.05
Sulfide	1
Nitrogen (total)	10
Temperature increase	less than or equal to 3°C[1]

[1] The effluent should result in a temperature increase of no more than 3 degrees Celsius at the edge of the zone where initial mixing and dilution takes place. Where the zone is not defined, use 100 meters from the point of discharge.

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

Solid Wastes and Sludges

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

The emission guidelines given here can be consistently achieved by well-designed, well-operated and well-maintained pollution control systems.

Ambient Noise

Noise abatement measures should achieve either the following levels or a maximum increase in background levels of 3 dB(A). Measurements are to be taken at noise receptors located outside the project property boundary.

Ambient Noise

	Maximum Allowable L_{eq} (hourly), in dB(A)	
Receptor	Daytime 07:00 - 22:00	Nighttime 22:00 - 07:00
Residential; institutional; educational	55	45
Industrial; commercial	70	70

The emission requirements given here can be consistently achieved by well-designed, well-operated and well-maintained pollution control systems.

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 above should be as detailed 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 SO_x, NO_x, and 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 8 hours for all the parameters cited above except for metals which should be monitored on at least a monthly basis.

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. These should be reported to the responsible authorities and relevant parties, as required, and provided to MIGA if requested.

Key Issues

The following box summarizes the key production and control practices that will lead to compliance with emission guidelines:

- Implement an equipment maintenance program which minimizes releases of volatile organics including ethylene oxide, benzene, vinyl chloride, 1,2-dichloroethane, and other organics.
- Install vapor recovery systems to reduce VOC emissions.

- Use low NO_x burners.
- Optimize fuel usage.
- Regenerate and reuse spent catalysts, solvents, and other spent solutions to the extent feasible.
- Recycle cooling water and reuse wastewaters.
- Segregate storm water from process wastewater.
- Use non-chrome based additives in cooling water.
- Design and practice emergency preparedness and prevention measures.

Further Information

The following are suggested as sources of additional information (these sources are provided for guidance and are not intended to be comprehensive):

Bounicore and Davis. 1992. *Air Pollution Engineering Manual*. New York: Van Nostrand Reinhold Publications.

Cortes, M. and Peter Bocock. 1984. North-South Technology Transfer, A Case Study of Petrochemicals in Latin America. Published for The World Bank by The John Hopkins University Press, Baltimore, Maryland.

The Economist Intelligence Unit. 1991. Petrochemicals - An Industry and Its Future by Roger Langley. Special Report No. 2067.

Her Majesty's Inspectorate of Pollution. 1993. Chief Inspector's Guidance to Inspectors, Environmental Protection Act 1990, Process Guidance Note IPR 4/1, Petrochemical Processes.

National Swedish Environmental Protection Board. 1987. Focus on Environmental Impacts of Petrochemical Plants in Stenungsund. SNV Report Number 3209.

The United Nations Industrial Development Organization (UNIDO). 1994. Report on Consultation on Downstream Petrochemical Industries in Developing Countries in Tehran, Islamic Republic of Iran during November 7 through 11, 1993.

The World Bank. 1990. The Petrochemicals Industry in Developing Asia, A Review of the Current Situation and Prospects for Development in the 1990s by Walter Vergara and Dominique Babelon. World Bank Technical Paper Number 113, Industry and Energy Series. Washington, DC.

The World Bank. 1988. The New Face of the World Petrochemical Sector, Implications for Developing Countries by Walter Vergara and Donald Brown. World Bank Technical Paper Number 84, Industry and Energy Series, Washington, DC.

ANNEX: Typical Processes and Products

C_1 compounds (having one carbon atom in their molecule) manufactured at petrochemical plants include methanol, formaldehyde, and halogenated hydrocarbons. Formaldehyde is used for the manufacture of plastic (including phenolic, urea, and melamine) resins. Halogenated hydrocarbons are used for 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, since it has three carbon atoms), butadiene, (C_4, since it has four carbon atoms) and in some cases, acetylene. The olefins manufactured are used for the manufacture of polyethylene (including low density polyethylene (LDPE) and high density polyethylene (HDPE)), 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 solvent and in cosmetics), isopropanol (used as solvent and in pharmaceuticals manufacturing), acrylonitrile (for 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 C4 compounds (having four carbon atoms) manufactured include butanol (used for the manufacture of solvents such as methyl ethyl ketone).

The major aromatics (organics with at least one ring structure with six carbon atoms) manufactured include benzene, toluene, xylene, and in some cases, 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 caprolactum (used in the manufacture of Nylon). Benzene is also used as a solvent.

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

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

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