

# Environmental, Health and Safety Guidelines for Large Volume Petroleum-based Organic Chemicals Manufacturing

## Introduction

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

The EHS Guidelines contain the performance levels and measures that are generally considered to be achievable in new facilities by existing technology at reasonable costs. Application of the EHS Guidelines to existing facilities may involve the establishment of site-specific targets, with an appropriate timetable for achieving them. The applicability of the EHS Guidelines should be tailored to the hazards and risks established for each project on the basis of the results of an

<sup>1</sup> 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.

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.

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

## Applicability

The EHS Guidelines for Large Volume Petroleum-based Organic Chemical Manufacturing include information relevant to large volume petroleum-based organic chemicals (LVOC) projects and facilities. They cover the production of following products:

- **Lower Olefins** from virgin naphtha, natural gas, and gas oil with special reference to ethylene and propylene and general information about main co-products [C4, C5

streams, pyrolytic gasoline (py-gas)), as valuable feedstock for organic chemicals manufacturing.

- **Aromatics** with special reference to the following compounds: benzene, toluene, and xylenes by extraction or extractive distillation from pyrolytic gasoline (py-gas); ethylbenzene and styrene by dehydrogenation, or oxidation with propylene oxide co-production; and cumene and its oxidation to phenol and acetone.
- **Oxygenated Compounds** with special reference to the following compounds: formaldehyde by methanol oxidation; MTBE (methyl t-butyl ether) from methanol and isobutene; ethylene oxide by ethylene oxidation; ethylene glycol by ethylene oxide hydration; and terephthalic acid by oxidation of p-xylene; acrylic esters by propylene oxidation to acrolein and acrylic acid plus acrylic acid esterification.
- **Nitrogenated Compounds** with special reference to the following compounds: acrylonitrile by propylene ammoxidation, with co-production of hydrogen cyanide; caprolactam from cyclohexanone; nitrobenzene by benzene direct nitration; and toluene diisocyanate (TDI) from toluene.
- **Halogenated Compounds** with special reference to the following compounds: ethylene dichloride (EDC) by ethylene chlorination and production of vinyl chloride (VCM) by dehydrochlorination of EDC as well by ethylene oxychlorination.

This document is organized according to the following sections:

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

## 1.0 Industry-Specific Impacts and Management

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

### 1.1 Environmental

Potential environmental issues associated with LVOC manufacturing include the following:

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

#### Air Emissions

Emission sources from chemical processes include process tail gases, heaters and boilers; valves, flanges, pumps, and compressors; storage and transfer of products and intermediates; waste water handling; and emergency vents and flares.

Industry-specific pollutants that may be emitted from point or fugitive sources during routine operations consist of numerous organic and inorganic compounds, including sulfur oxides (SO<sub>x</sub>), ammonia (NH<sub>3</sub>), ethylene, propylene, aromatics, alcohols, oxides, acids, chlorine, EDC, VCM, dioxins and furans, formaldehyde, acrylonitrile, hydrogen cyanide, caprolactam, and other volatile organic compounds (VOCs) and semivolatile organic compounds (SVOC).

Air quality impacts should be estimated by the use of baseline air quality assessments and atmospheric dispersion models to establish potential ground-level ambient air concentrations during facility design and operations planning as described in the **General EHS Guidelines**. These studies should ensure that no adverse impacts to human health and the environment result.

Combustion sources for power generation are common in this industry sector. Guidance for the management of small combustion source emissions with a capacity of up to 50 megawatt hours thermal (MWth), including air emission standards for exhaust emissions, is provided in the **General EHS Guidelines**. Guidance applicable to emissions sources greater than 50 MWth are presented in the EHS Guidelines for Thermal Power.

#### *Process Emissions from Lower Olefins Production*

Typically, the olefins plants are part of an integrated petrochemical and/or refining complex and are frequently used to recover vent and purge streams from other units (e.g., polymer manufacturing plants). Process emissions are mainly the following:

- Periodic decoking of cracking furnaces to remove carbon build-up on the radiant coils. Decoking produces significant particulate emissions and carbon monoxide;
- Flare gas systems to allow safe disposal of any hydrocarbons or hydrogen that cannot be recovered in the process (i.e., during unplanned shutdowns and during start-ups). Crackers typically have at least one elevated flare as well as some ground flares; and
- VOC emissions from pressure relief devices, venting of off-specification materials or depressurizing and purging of equipment for maintenance. Crack gas compressor and refrigeration compressor outages are potential sources of short-term, high rate VOC emissions. During normal

operation, VOC emissions from the cracking process are usually reduced because they are recycled, used as fuel or routed to associated processes in an integrated site. Elevated VOC emissions from ethylene plants are intermittent, and may occur during plant start-up and shutdown, process upsets, and emergencies.

Recommended emission prevention and control measures include the following:

- Implementing advanced multi-variable control and on-line optimization, incorporating on-line analyzers, performance controls, and constraint controls;
- Recycling and/or re-using hydrocarbon waste streams for heat and steam generation;
- Minimizing the coke formation through process optimization;
- Use of cyclones or wet scrubbing systems to abate particulate emissions;
- Implementing process control, visual inspection of the emission point, and close supervision of the process parameters (e.g., temperatures) during the de-coking phase;
- Recycling the decoking effluent stream to the furnace firebox where sufficient residence time permits total combustion of any coke particles;
- Flaring during startup should be avoided as much as possible (flareless startup);
- Minimizing flaring during operation<sup>2</sup>;
- Collecting emissions from process vents and other point sources in a closed system and routing to a suitable purge gas system for recovery into fuel gas or to flare;
- Adopting closed loop systems for sampling;

<sup>2</sup> The normally accepted material loss for good operating performance is around 0.3 - 0.5 % of hydrocarbon feed to the plant (5 to 15 kg hydrocarbons/tonne ethylene).

- Hydrogen sulfide generated in sour gas treatment should be burnt to sulfur dioxide or converted to sulfur by Claus unit;
- Installing permanent gas monitors, video surveillance and equipment monitoring (such as on-line vibration monitoring) to provide early detection and warning of abnormal conditions; and
- Implementing regular inspection and instrument monitoring to detect leaks and fugitive emissions to atmosphere (Leak Detection and Repair (LDAR) programs).

### *Process Emissions from Aromatics Production*

Emissions from aromatics plants are to a large extent due to the use of utilities (e.g., heat, power, steam, and cooling water) needed by the aromatics separation processes. Emissions related to the core process and to the elimination of impurities include:

- Vents from hydrogenations (pygas hydrostabilization, cyclohexane reaction) may contain hydrogen sulfide (from the feedstock desulphurization), methane, and hydrogen;
- Dealkylation off-gases;
- VOC (e.g., aromatics (benzene, toluene), saturated aliphatics (C1–C4) or other aliphatics (C2–C10)) emissions from vacuum systems, from fugitive sources (e.g., valve, flange and pump seal leaks), and from non-routine operations (maintenance, inspection). Due to lower operating temperatures and pressures, the fugitive emissions from aromatics processes are often less than in other LVOC manufacturing processes where higher temperatures and pressures are needed;
- VOC emissions from leaks in the cooling unit when ethylene, propylene, and/or propane are used as coolant fluids in the p-xylene crystallization unit;

- VOC emissions from storage tank breathing losses and displacement of tanks for raw materials, intermediates, and final products.

Recommended emission prevention and control measures include the following:

- Routine process vents and safety valve discharges should preferably be conveyed to gas recovery systems to minimize flaring;
- Off-gas from hydrogenations should be discharged to a fuel gas network and burnt in a furnace to recover calorific value;
- Dealkylation off-gases should be separated in a hydrogen purification unit to produce hydrogen (for recycle) and methane (for use as a fuel gas);
- Adopting closed loop sample systems to minimize operator exposure and to minimize emissions during the purging step prior to taking a sample;
- Adopting 'heat-off' control systems to stop the heat input and shut down plants quickly and safely in order to minimize venting during plant upsets;
- Where the process stream contains more than 1 weight percent (wt%) benzene or more than 25 wt% aromatics, use closed piping systems for draining and venting hydrocarbon containing equipment prior to maintenance; and use canned pumps or, where they are not applicable, single seals with gas purge or double mechanical seals or magnetically driven pumps;
- Minimizing fugitive leaks from rising stem manual or control valve fittings with bellows and stuffing box, or using high-integrity packing materials (e.g., carbon fiber);
- Using compressors with double mechanical seals, or a process-compatible sealing liquid, or a gas seal;

- Using double seal floating roof tanks or fixed roof tanks incorporating an internal floating rood with high integrity seals; and
- Loading or discharging of aromatics (or aromatics-rich streams) from road tankers, rail tankers, ships and barges should be provided with a closed vent systems connected to a vapor recovery unit, to a burner, or to a flare system.

### *Process Emissions from Oxygenated Compounds Production*

#### **Formaldehyde**

Primary sources of formaldehyde process emissions are the following:

- Purged gases from the secondary absorber and the product fractionator in the silver process;
- Vented gases from the product absorber in the oxide process;
- A continuous waste gas stream for both the silver and oxide processes from the formaldehyde absorption column; and
- Fugitive emissions and emissions arising from breathing of storage tanks.

Typically, waste gases from the silver process should be treated thermally. Waste gases from the oxide process and from materials transfer and breathing of storage tanks should be treated catalytically.<sup>3</sup> Specific recommended emission prevention and control measures include the following:

- Connection of vent streams from absorber, storage and loading/unloading systems to a recovery system (e.g., condensation, water scrubber) and/or to a vent gas treatment (e.g., thermal/catalytic oxidizer, central boiler plant);

- Abatement of the absorber off-gases in the silver process with gas engines and dedicated thermal oxidation with steam generation;
- Treatment of reaction off-gas from the oxide process with a dedicated catalytic oxidation system; and
- Minimization of vent streams from storage tanks by back-venting on loading/unloading and treating the polluted streams by thermal or catalytic oxidation, adsorption on activated carbon (only for methanol storage vents), absorption in water recycled to the process, or connection to the suction of the process air blower (only for formaldehyde storage vents).

#### **MTBE (methyl t-butyl ether)**

MTBE has a vapor pressure of 61 kPa at 40 °C, and an odor threshold of 0.19 mg/m<sup>3</sup>. Fugitive emissions from storage facilities should be controlled and prevented adopting appropriate design measures for storage tanks.

#### **Ethylene Oxide/Ethylene Glycol**

The main air emissions from ethylene oxide (EO)/ethylene glycol (EG) plants are the following<sup>4</sup>:

- Carbon dioxide, as a by-product during the manufacture of EO, removed by absorption in a hot carbonate solution, and then stripped and vented to air with minor quantities of ethylene and methane;
- Purge gas from recycle gas to reduce the build-up of inert gases and vented to air after treatment. In the oxygen based process, the purge gas consists mainly of hydrocarbons (e.g., ethylene, methane, etc.) and inert gases (mainly nitrogen and argon impurities present in the ethylene and oxygen feedstock). After treatment, the

<sup>3</sup> EIPPCB BREF (2003)

<sup>4</sup> Ibid.

- remaining gases (mainly nitrogen and carbon dioxide) are vented to atmosphere;
- VOC and some compounds with lower volatility (due to mechanical entrainment) from open cooling towers where EO-solution is stripped, cooled and re-routed to the absorber;
  - EO containing non-condensable gases like argon, ethane, ethylene, methane, carbon dioxide, oxygen, and/or nitrogen vent gases from various sources in the process (e.g., flashing steps in the EO recovery section, EO purification section, process analyzers, safety valves, EO storage or buffer vessels, and EO loading / unloading operations);
  - Fugitive emissions with VOC releases of EO, ethylene, and methane (where methane is applied as diluent in the recycle gas loop).
- Adoption of high-integrity sealing systems for pumps, compressors, and valves and use of proper types of O-ring and gasket materials;
  - Adoption of a vapor return system for EO loading to minimize the gaseous streams requiring further treatment. Displaced vapors from the filling of tankers and storage tanks should be recycled either to the process or scrubbed prior to incineration or flaring. When the vapors are scrubbed (e.g., vapors with low content in methane and ethylene), the liquid effluent from the scrubber should be routed to the desorber for EO recovery;
  - Minimization of the number of flanged connections, and installation of metal strips around flanges with vent pipes sticking out of the insulation to allow monitoring of EO release; and
  - Installation of EO and ethylene detection systems for continuous monitoring of ambient air quality.

Recommended emission prevention and control measures include the following:

- Favoring direct oxidation of ethylene by pure oxygen due to the lower ethylene consumption and lower off-gas production;
- Optimization of the hydrolysis reaction of EO to glycols in order to maximize the production of glycols, and to reduce the energy (steam) consumption;
- Recovery of absorbed ethylene and methane from the carbonate solution, prior to carbon dioxide removal, and recycling back to the process. Alternatively, they should be removed from the carbon dioxide vent either by thermal or catalytic oxidizers;
- Inert gas vent should be used as a fuel gas, where possible. If their heating value is low, they should be routed to a common flare system to treat EO emissions;

#### **Terephthalic Acid (TPA) / Dimethyl Terephthalate (DMT)**

Gaseous emissions include off-gases from the oxidation stage and other process vents. Because volumes of potential emissions are typically large and include such chemicals as p-xylene, acetic acid, TPA, methanol, methyl p-toluate, and DMT, off gases should be effectively recovered, pre-treated (e.g., scrubbing, filtration) if necessary depending on the gas stream, and incinerated.

#### *Process Emissions from Nitrogenated Compounds Production*

##### **Acrylonitrile<sup>5</sup>**

Emission sources include gaseous vent streams from the core process plant, reactor off-gases absorber streams (saturated with water, and containing mainly nitrogen, unreacted propylene, propane, CO, CO<sub>2</sub>, argon, and small amounts of

<sup>5</sup> EIPPCB BREF (2003)

reaction products), crude acrylonitrile run and product storage tanks, and fugitive emissions from loading and handling operations.

Recommended emission prevention and control measures include the following:

- Gaseous vent streams from the core process plant should be flared, oxidized (thermally or catalytically), scrubbed, or sent to boilers or power generation plants (provided combustion efficiency can be ensured). These vent streams are often combined with other gas streams;
- Reactor off-gases absorber streams, after ammonia removal, should be treated by thermal or catalytic oxidation, either in a dedicated unit or in a central site facility; and
- Acrylonitrile emission from storage, loading, and handling should be prevented using internal floating screens in place of fixed roof tanks as well as wet scrubbers.

### Caprolactam

Main emissions from caprolactam production include the following:

- A vent gas stream, produced in crude caprolactam extraction, containing traces of organic solvent;
- Cyclohexanone, cyclohexanol, and benzene from the cyclohexanone plant;
- Cyclohexane from tank vents and vacuum systems from the HPO plant;
- Cyclohexanone and benzene from tank vents and vacuum systems from HSO plant;
- Vents from aromatic solvent, phenol, ammonia, and oleum (i.e., fuming sulfuric acid - a solution of sulfur trioxide in sulfuric acid) storage tanks; and

- Nitrogen oxides and sulfur oxides (the latter in HSO plants) from catalytic NO<sub>x</sub> treatment units.

Recommended emission prevention and control measures include the following:

- Treatment of organic solvent laden streams by carbon adsorption;
- Recycling of waste gases from the HPO and HSO plants as fuel while minimizing flaring;
- Waste gases with nitric oxide and ammonia should be treated catalytically;
- Aromatic solvent tanks should be connected to a vapor destruction unit;
- Vents of oleum, phenol and ammonia storage tanks should be equipped with water scrubbers; and
- Balancing lines should be used to reduce losses from loading and unloading operations.

### Nitrobenzene

The main air emissions from nitrobenzene production include vents from distillation columns and vacuum pumps, vents from storage tanks, and emergency venting from safety devices. All process and fugitive emissions should be prevented and controlled as described in previous sections.

### Toluene Diisocyanate<sup>6</sup>

The hazardous nature of toluene diisocyanate (TDI) and the other associated intermediates, line products, and by-products requires a very high level of attention and prevention.

Generally, the waste gas streams from all processes (manufacture of dinitrotoluene (DNT), toluene-diamine (TDA), and TDI) are treated to remove organic or acidic compounds.

<sup>6</sup> EIPPCB BREF (2003)

Most of the organic load is eliminated by incineration. Scrubbing is used to remove acidic compounds or organic compounds at low concentration. Recommended emission prevention and control measures include the following:

- Nitric acid storage tank vent emissions should be recovered with wet scrubbers and recycled;
- Organic liquid storage tank vent emissions should be recovered or incinerated;
- Emissions from nitration reactor vents should be scrubbed or destroyed in a thermal or catalytic incinerator;
- Nitrogen oxide emissions and VOC emissions of a DNT plant should be reduced by selective catalytic reduction;
- Isopropylamine and/or other light compounds formed by a side reaction when isopropanol is used should be incinerated;
- Off-gases from phosgenation, containing phosgene, hydrogen chloride, o-dichlorobenzene solvent vapors, and traces of TDI, should be recycled to the process if possible. Where this is not practical, o-dichlorobenzene and phosgene should be recovered in chilled condensers. Phosgene should be recycled; residues should be destroyed with caustic soda and effluent gases should be incinerated;
- Hydrogen chloride evolved from the 'hot' phosgenation stage should be recovered by scrubbers with >99.9% efficiency;
- Phosgene in the crude product from 'hot' phosgenation should be recovered by distillation;
- Waste gas with low concentrations of diisocyanates should be treated by aqueous scrubbing;
- Unrecovered phosgene should be decomposed with alkaline scrubbing agents through packed towers or activated carbon towers. Residual gases should be combusted to convert phosgene to CO<sub>2</sub> and HCl. Outlet

gas from should be continuously monitored for residual phosgene content;

- Selection of resistant, high-grade materials for equipment and lines, careful testing of equipment and lines, leak tests, use of sealed pumps (canned motor pumps, magnetic pumps), and regular inspections of equipment and lines; and
- Installation of continuously operating alarm systems for air monitoring, systems for combating accidental release of phosgene by chemical reaction (e.g., steam ammonia curtains in the case of gaseous emissions), jacketed pipes, and complete containment for phosgene plant units.

#### *Process Emissions from Halogenated Compounds Production*

The main emissions from halogenated compound production lines are the following:

- Flue gas from thermal or catalytic oxidation of process gases and from incineration of liquid chlorinated wastes;
- VOC emissions from fugitive sources such as valves, flanges, vacuum pumps, and wastewater collection and treatment systems and during process maintenance;
- Process off-gases from reactors and distillation columns;
- Safety valves and sampling systems; and
- Storage of raw materials, intermediates, and products.

Recommended emission prevention and control measures include the following<sup>7,8</sup>:

<sup>7</sup> The Oslo and Paris Commission (OSPAR) issued Decision 98/4 on achievable emission levels from 1,2 dichloroethane (EDC)/vinyl chloride monomer (VCM) manufacture. The decision is based on a BAT technical document (PARCOM, 1996) and a BAT Recommendation (PARCOM, 1996).

<sup>8</sup> The European Council of Vinyl Manufacturers (ECVM) issued in 1994 an industry charter to improve environmental performance and introduce emission levels that were considered achievable on EDC/VCM units. The ECVM charter identifies techniques that represent good practice in the processing, handling, storage and transport of primary feedstock and final products in VCM manufacture.

- Consider the use of direct chlorination at high temperature to limit emission and waste production;
- Consider the use of oxychlorination fluidized bed reactors to reduce by-products formation;
- Use oxygen, selective hydrogenation of acetylene in the feed, improved catalysts, and reaction optimization;
- Implement LDAR (leak detection and repair) programs;
- Preventing leaks from relief vents, using rupture disks in combination safety valves with pressure monitoring between the rupture disc and the safety valves to detect any leaks;
- Installation of vapor return (closed-loop) systems to reduce ethylene dichloride (1,2 dichloroethane; EDC)/vinyl chloride monomer (VCM) emissions when loading and pipe connections for loading/unloading are fully evacuated and purged before decoupling. The system should allow gas recovery or be routed to a thermal / catalytic oxidizer with a hydrochloric acid (HCl) absorption system. Where practical, organic residues should be re-used as feedstock for chlorinated solvent processes (tri-per or tetra-per units);
- Atmospheric storage tanks for EDC, VCM, and chlorinated by-products should be equipped with refrigerated reflux condensers or vents to be connected to gas recovery and reuse and/or a thermal or catalytic oxidizer with HCl absorption system; and
- Installation of vent condensers / vent absorbers with recycling of intermediates and products.

### *Venting and Flaring*

Venting and flaring are important operational and safety measures used in LVOC facilities to ensure that vapors gases are safely disposed of. Typically, excess gas should not be vented, but instead sent to an efficient flare gas system for disposal. Emergency venting may be acceptable under specific

conditions where flaring of the gas stream is not possible, on the basis of an accurate risk analysis and integrity of the system needs to be protected. Justification for not using a gas flaring system should be fully documented before an emergency gas venting facility is considered.

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

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

- Implementation of source gas reduction measures to the maximum extent possible;
- Use of efficient flare tips, and optimization of the size and number of burning nozzles;
- Maximizing flare combustion efficiency by controlling and optimizing flare fuel / air / steam flow rates to ensure the correct ratio of assist stream to flare stream;
- Minimizing flaring from purges and pilots, without compromising safety, through measures including installation of purge gas reduction devices, flare gas recovery units, inert purge gas, soft seat valve technology where appropriate, and installation of conservation pilots;
- Minimizing risk of pilot blow-out by ensuring sufficient exit velocity and providing wind guards;
- Use of a reliable pilot ignition system;

- Installation of high-integrity instrument pressure protection systems, where appropriate, to reduce over pressure events and avoid or reduce flaring situations;
- Installation of knock-out drums to prevent condensate emissions, where appropriate;
- Minimizing liquid carry-over and entrainment in the gas flare stream with a suitable liquid separation system;
- Minimizing flame lift off and / or flame lick;
- Operating flare to control odor and visible smoke emissions (no visible black smoke);
- Locating flare at a safe distance from local communities and the workforce including workforce accommodation units;
- Implementation of burner maintenance and replacement programs to ensure continuous maximum flare efficiency;
- Metering flare gas.

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

### *Dioxins and Furans*

Waste incineration plants are typically present as one of the auxiliary facilities in LVOC facilities. The incineration of chlorinated organic compounds (e.g., chlorophenols) could generate dioxins and furans. Certain catalysts in the form of transition metal compounds (e.g., copper) also facilitate the formations of dioxins and furans. Recommended prevention and control strategies include:

- Operating incineration facilities according to internationally recognized technical standards;<sup>9</sup>

- Maintaining proper operational conditions, such as sufficiently high incineration and flue gas temperatures, to prevent the formation dioxins and furans;
- Ensuring emissions levels meet the guideline values presented in Table 1.

## **Wastewater**

### *Industrial process wastewater*

Liquid effluents typically include process and cooling water, storm water, and other specific discharges (e.g., hydrotesting, washing and cleaning mainly during facility start up and turnaround). Process wastewater includes:

### *Effluents from Lower Olefins Production*

Effluents from steam crackers and relevant recommended prevention and control measures are the following:

- Steam flow purges (typically 10 percent of the total dilution steam flow used to prevent contaminant build-up) should be neutralized by pH adjustment and treated via an oil/water separator and air-flotation before discharge to the facility's wastewater treatment system;
- Spent caustic solution, if not reused for its sodium sulfide content or for cresol recovery, should be treated using a combination of the following steps:
  - Solvent washing or liquid-liquid extraction for polymers and polymer precursors;
  - Liquid-liquid settler and/or coalescer for removing and recycling the free liquid gasoline phase to the process;
  - Stripping with steam or methane for hydrocarbon removal;
  - Neutralization with a strong acid (which results in a H<sub>2</sub>S / CO<sub>2</sub> gas stream that is combusted in a sour gas flare or incinerator);

<sup>9</sup> For example, Directive 2000/76/EC

- Neutralization with acid gas or flue gas (which will partition the phenols into a buoyant oily phase for further treatment);
- Oxidation (wet air or catalytic wet air or ozone) to oxidize carbon and sulfides/mercaptans before neutralization (to reduce or eliminate H<sub>2</sub>S generation).
- Spent amine solution, used to remove hydrogen sulfide from heavy feedstock in order to reduce the amount of caustic solution needed for final process gas treatment. The used amine solution should be regenerated by steam stripping to remove hydrogen sulfide. A portion of the amine wash is bled off to control the concentration of accumulating salts; and
- A stream of C<sub>2</sub> polymerization product known as 'green oil' produced during acetylene catalytic hydrogenation to ethylene and ethane, containing multi-ring aromatics (e.g. anthracene, chrysene, carbazole). It should be recycled into the process (e.g., into the primary fractionator for recovery as a component of fuel oil) or should be burnt for heat recovery.

### *Effluents from Aromatics Production*

Process water within aromatics plants is generally operated in closed loops. The main wastewater sources are process water recovered from condensates of the steam jet vacuum pumps and overhead accumulators of some distillation towers. These streams contain small quantities of dissolved hydrocarbons. Wastewater containing sulfide and COD may also be generated from caustic scrubbers. Other potential sources are unintentional spillages, purge of cooling water, rainwater, equipment wash-water, which may contain extraction solvents and aromatics and water generated by tank drainage and process upsets.

Wastewater containing hydrocarbons should be collected separately, settled and steam stripped prior to biological treatment in the facility's wastewater treatment systems.

### *Effluents from Oxygenated Compounds Production*

#### **Formaldehyde**

Under routine operating conditions, the silver and oxide processes do not produce significant continuous liquid waste streams. Effluents may arise from spills, vessel wash-water, and contaminated condensate (e.g., boiler purges and cooling water blow down that are contaminated by upset conditions such as equipment failure). These streams can be recycled back into the process to dilute the formaldehyde product.

#### **Ethylene Oxide/Ethylene Glycol**

A bleed stream from the process is rich in organic compounds, mainly mono-ethylene glycol (MEG), di-ethylene glycol (DEG) and higher ethylene glycols, but also with minor amounts of organic salts. The effluent stream should be routed to a glycol plant (if available) or to a dedicated unit for glycol recovery and partial recycle of water back to the process. The stream should be treated in a biological treatment unit, as ethylene oxide readily biodegrades.

#### **Terephthalic Acid/Dimethyl Terephthalate**

Effluents from the terephthalic acid process include water generated during oxidation and water used as the purification solvent. Effluents are usually sent to aerobic wastewater treatment, where the dissolved species, mostly terephthalic acid, acetic acid, and impurities such as p-toluic acid, are oxidized to carbon dioxide and water. Alternatively, anaerobic treatment with methane recovery can be considered. Waste streams from distillation in the dimethyl terephthalate process can be burnt for energy recovery.

### Acrylic Esters

Liquid wastes are originated at different stages of production. In acrylic acid purification, a small aqueous phase is purged from the distillation after the extraction step. This aqueous material should be stripped before disposal both to recover extraction solvent and minimize waste organic disposal loads.

Bottoms from the acrylic acid product column should be stripped to recover acrylic acid, whereas the high boiling organic compounds are burnt.

Organic and sulfuric wastes are produced from the esterification reactor. Aqueous wastes are produced from alcohol stripping in diluted alcohol recovery. Organic heavy wastes are produced in the final ester distillation. The aqueous column bottoms should be incinerated or sent to biological treatment. Organic heavy wastes should be incinerated.

### *Effluents from Nitrogenated Compounds Production*

#### **Acrylonitrile<sup>10</sup>**

Various aqueous streams are generated from this unit. They are normally sent to the facility's biological treatment system with at least 90 percent abatement. They include the following:

- A purge stream of the quench effluent stream(s) containing a combination of ammonium sulfate and a range of high-boiling organic compounds in an aqueous solution. Ammonium sulfate can be recovered as a crystal co-product or treated to produce sulfuric acid. The remaining stream containing heavy components should be treated to remove sulfur and then incinerated or biologically treated. The stream containing the light components should be biologically treated or recycled to the plant; and

- Stripping column bottoms, containing heavy components and excess water produced in the reactors. The aqueous stream should be treated by evaporative concentration; the distillate should be biologically treated and the concentrated heavy stream is burnt (with energy recovery) or recycled.

#### **Caprolactam**

The liquid effluents from this production plant include the following:

- Heavy bottoms from crude caprolactam extraction, in all processes using Beckmann rearrangement, containing ammonium sulfate and other sulfur compounds, which should be processed into sulfuric acid; and
- A residue of finished caprolactam distillation, which should be incinerated.

#### **Nitrobenzene<sup>11</sup>**

The nitration process is associated with the disposal of wastewater from the neutralization and washing steps and from reconcentration of sulfuric acid. This water can contain nitrobenzene, mono- and polynitrated phenolics, carboxylic acids, other organic by-products, residual base, and inorganic salts from the neutralized spent acid that was present in the product.

Recommended pollution prevention and control measures include the following:

- Neutralization of the organic phase with alkalis;
- Extraction of the acidic contaminants from the organic phase using molten salts (e.g., mixture of zinc nitrate and magnesium nitrate). Salts are then regenerated by flashing

<sup>10</sup> EIPPCB BREF (2003)

<sup>11</sup> Kirk-Othmer (2006)

off nitric acid. If necessary, the organic phase can undergo a polishing neutralization;

- The acidic contaminants can alternatively be removed by employing a system that utilizes solvent (e.g., benzene) extractions, precipitation, distillation, and other treatments. Residual nitric acid can be removed by a multistage countercurrent liquid-liquid extraction, and then reconcentrated by distillation for further use;
- Multistage countercurrent solvent extraction and steam stripping, usually combined. These methods can extract up to 99.5% of nitrobenzene from the wastewater, but they leave any nitrophenols or picric acids in the water. Concentrated extracts should be treated to recovery or sent to incineration; and
- Thermal pressure decomposition for removal of nitrophenols and picric acid in the wastewater stream coming from alkaline washing. After stripping of residual nitrobenzene and benzene, wastewater should be heated up to 300 °C at a pressure of 100 bars;

### **Toluene Diisocyanate<sup>12</sup>**

Wastewater is produced from toluene nitration with inorganic components (sulfate and nitrite / nitrate) and organic products and by-products, namely di- and trinitrocresols.

Recommended pollution prevention and control measures include the following:

- Optimization of the process can give emissions of <10 kg nitrate/ t DNT and much lower content of nitrite, before further removal by the biological treatment. Alternative techniques to reduce the organic load of the effluents from the nitration process are adsorption, extraction or stripping, thermolysis/hydrolysis or oxidation. Extraction (e.g. with

toluene), which is the most commonly used technique, allows an almost complete removal of DNT and a reduction of nitrocresols to <0.5 kg/t;

- In toluene diamine preparation ammonia can be separated by stripping. Low-boiling components can be separated by distillation / stripping with steam and destroyed by incineration. Pre-treated process water can be re-used in the production process. Isopropanol, where used, can be recovered for re-use. Any isopropanol in scrubber effluents can be biologically treated;
- In phosgenation of toluene diamines, slightly acidic effluents from off-gas decomposition towers, containing traces of o-dichlorobenzene solvent, can be biologically treated or sent to a combustor with heat recovery and neutralization of halogenated effluents; and
- The TDI process produces water in the nitration and hydrogenation steps. Key treatment steps normally involve concentrating the contaminants in the water stream using evaporation (either single or multiple effects), recycling, or burning. The treated water stream recovered from these concentration processes should be further treated in the facility's biological wastewater treatment systems prior to discharge.

### *Effluents from Halogenated Compounds Production<sup>13</sup>*

EDC/VCM plants have specific effluent streams from wash water and condensate from EDC purification (containing VCM, EDC, other volatile chlorinated hydrocarbons and non-volatile chlorinated material such as chloral or chloroethanol), oxychlorination reaction water, water seal flushes from pumps, vacuum pumps and gas-holders, cleaning water from maintenance operations and intermittent aqueous phase from the storage of crude (wet) EDC and light-ends. The main compounds in these effluents are the following:

<sup>12</sup> EIPPCB BREF (2003)

<sup>13</sup> EIPPCB BREF (2003)

- 1,2 dichloroethane (EDC) and other volatile chlorinated organic compounds;
- Non-volatile chlorinated organic compounds;
- Other organic compounds, such as sodium formate glycol;
- Copper catalyst (when oxychlorination uses fluidized-bed technology); and
- Dioxin related components (with a strong affinity to catalyst particles).

Recommended pollution prevention and control measures include the following:

- Use of boiling reactors for direct chlorination to produce EDC in vapor form, reducing the need to remove catalyst from the effluent and EDC product;
- Steam or air stripping of volatile chlorinated organic compounds such as EDC, VCM, chloroform, and carbon tetrachloride. The stripped compounds can be recycled to the process. Stripping can be performed at atmospheric pressure, under pressure, or under vacuum;
- Alkaline treatment to convert non-volatile oxychlorination by-products (e.g., chloral or 2-chloroethanol) into compounds that can be stripped (e.g., chloroform) or are degradable (e.g., ethylene glycol, sodium formate);
- Removal of the entrained copper catalyst from the oxychlorination process by alkaline precipitation and separation by settling/flocculation and sludge recovery; and
- Dioxins and related compounds (PCDD/F), generated during oxychlorination fluid bed technology are partly removed in the copper precipitation, together with the catalyst residues (metal sludge). Additional removal of PCDD/F related compounds can be achieved by flocculation and settling or filtration followed by biological treatment. Adsorption on activated carbon can also be used as additional treatment.

### *Hydrostatic Testing-Water*

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

- Using the same water for multiple tests;
- Reducing the need for corrosion inhibitors and other chemicals by minimizing the time that test water remains in the equipment or pipeline;
- If chemical use is necessary, selecting the least hazardous alternative with regards to toxicity, biodegradability, bioavailability, and bioaccumulation potential.

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

### *Process Wastewater Treatment*

Techniques for treating industrial process wastewater in this sector include source segregation and pretreatment of concentrated wastewater streams. Typical wastewater treatment steps include: grease traps, skimmers, dissolved air floatation or oil water separators for separation of oils and floatable solids; filtration for separation of filterable solids; flow and load equalization; sedimentation for suspended solids reduction using clarifiers; biological treatment, typically aerobic treatment, for reduction of soluble organic matter (BOD); chlorination of effluent when disinfection is required; and dewatering and

disposal of residuals in designated hazardous waste landfills. Additional engineering controls may be required for (i) containment and treatment of volatile organics stripped from various unit operations in the wastewater treatment system, (ii) advanced metals removal using membrane filtration or other physical/chemical treatment technologies, (iii) removal of recalcitrant organics and non biodegradable COD using activated carbon or advanced chemical oxidation, (iii) reduction in effluent toxicity using appropriate technology (such as reverse osmosis, ion exchange, activated carbon, etc.), and (iv) containment and neutralization of nuisance odors.

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

### *Other Wastewater Streams & Water Consumption*

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

### **Hazardous Materials**

LVOC manufacturing facilities use and manufacture significant amounts of hazardous materials, including raw materials and intermediate/final products. The handling, storage, and transportation of these materials should be managed properly to avoid or minimize the environmental impacts. Recommended practices for hazardous material management, including

handling, storage, and transport, as well as issues associated with Ozone Depleting Substances (ODSs) are presented in the **General EHS Guidelines**.

### **Wastes and Co-products**

Well-managed LVOC production processes do not generate significant quantities of solid wastes during normal operation. The most significant solid wastes are spent catalysts, from their replacement in scheduled turnarounds of plants and by products.

Recommended management strategies for spent catalysts include the following:

- Proper on-site management, including submerging pyrophoric spent catalysts in water during temporary storage and transport to avoid uncontrolled exothermic reactions; and
- Off-site management by specialized companies that can either recover heavy metals (or precious metals), through recovery and recycling processes whenever possible, or manage spent catalysts according to industrial waste management recommendations included in the **General EHS Guidelines**.

Recommended management strategies for off spec products include recycling to specific production units for reutilization or disposal. Guidance on the storage, transport and disposal of hazardous and non-hazardous wastes is presented in the **General EHS Guidelines**.

### *Lower Olefins Production*

Limited quantities of solid waste are produced by steam cracking process, mainly organic sludge, spent catalysts, spent desiccants, and coke. Each waste should be treated on a case by case basis, and may be recycled, reclaimed or re-used after

treatment. Alternatively they may be incinerated or landfilled. Molecular sieve desiccants and acetylene hydrogenation catalysts may be regenerated and reused.

### *Aromatics Production*

There is no production of hazardous waste during normal operation and virtually all the feedstock is recovered into valuable products, or as fuel gas. The most significant solid wastes produced and methods for their treatment and disposal include the following:

- Spent catalyst from the liquid or gas phase hydrogenation of olefins/diolefins and sulfur are typically processed to separate the valuable metal for re-use;
- Clay from olefins removal disposed of in landfills or incinerated;
- Adsorbents from xylene separations consisting of alumina or molecular sieves disposed of in landfills;
- Sludge / solid polymerization material recovered from process equipment during maintenance activities incinerated or used on-site as a fuel source; and
- Oil contaminated materials and oily sludge (from solvents, bio-treatment and water filtration) incinerated with associated heat recovery.

### *Oxygenated Compounds Production*

#### **Formaldehyde**

There is negligible generation of solid wastes in the silver and oxide processes under normal operating conditions. Almost all of the spent catalysts from reactors and off-gas oxidation can be regenerated. A limited build-up of solid para-formaldehyde may occur (principally at cold spots in equipment and pipes) and is removed during maintenance activities. Spent filters may also be generated from the purification of formaldehyde product. In

the oxide process spent heat transfer fluid is most frequently sent to a reclaimer (for recycling) or to incineration.

#### **Ethylene Oxide/Ethylene Glycol**

Spent EO catalyst, consisting of finely distributed metallic silver on a solid carrier (e.g., alumina), is sent to an external reclaimer for recovery of the valuable silver. After silver reclamation, the inert carrier requires disposal.

Heavy glycol liquid residues can be either reused as such or fractionated to yield marketable glycols, in order to minimize the volume to be disposed of.

Liquid residue from EO recovery section can be distilled to give valuable glycols and a heavy residue containing salts (either for sale or incineration). The stream can also be reused without distillation.

#### **Terephthalic Acid/Dimethyl Terephthalate**

Limited amounts of impure TPA and DMT are originated from plant start-up and shutdown, or from maintenance operations. In addition, semisolid products can be originated as bottoms in distillation operations. These wastes can be incinerated.

#### **Acrylic Esters**

Process solid wastes from acrylic esters manufacture are spent oxidation catalysts from their replacement in scheduled turn-arounds, containing bismuth, molybdenum, vanadium, and possibly minor amounts of tungsten, copper, tellurium, and arsenic, supported on silica and polymer crusts. They are collected during maintenance operations of columns, strippers, vessels, and pipes.

## *Nitrogenated Compounds Production*

### **Acrylonitrile<sup>14</sup>**

Hydrogen cyanide co-product is produced in the acrylonitrile reactors and may be recovered as the overhead product from the purification train. The hydrogen cyanide is either reused or converted on-site to other products.

Acetonitrile co-product is produced in the acrylonitrile reactors and is separated as an overhead product from the stripper column. Hydrogen cyanide is also present in this stream.

Ammonium sulfate co-product is produced in the quench area of the process. The ammoxidation reaction takes place in fluid bed reactors and the catalyst is retained in the reactors using combinations of cyclones but some catalyst is lost and exits the process through the quench system.

Recommended management strategies include the following:

- Maximizing the re-use of hydrogen cyanide, acetonitrile, and ammonium sulfate byproducts;
- Incinerating hydrogen cyanide, if it cannot be recovered, in a flare or incinerator;
- Recovery of crude acetonitrile from the core unit for further purification. If recovery is not practical, burning the crude liquid acetonitrile stream or mixing the crude acetonitrile with the absorber vent stream for burning (with energy recovery);
- Recovery of ammonium sulfate as crystal, or, where recovery is not possible, conversion to sulfuric acid;
- Separation of the catalyst fines by settling or filtration and treatment by combustion or landfill disposal;
- Minimization of heavy residues by reducing the formation of fines and catalyst losses, avoiding degradation of

products by using mild operating conditions and addition of stabilizers; and

- Collection of heavy residues from the stripper column bottoms and/or from the quench system (basic quench) together with the catalyst fines, followed by on-site or off-site incineration.

### **Caprolactam**

Ammonium sulfate by-product is obtained from both oxidation and neutralization processes. It is typically reused as a fertilizer.

### **Toluene Diisocyanate**

Recovered hydrogenation catalyst is recycled after centrifugation. A fraction is purged from the process and may be regenerated by specialized companies, or incinerated or pre-treated prior to final disposal. Organic wastes from the manufacture of DNT, TDA, and TDI are usually incinerated.

## *Halogenated Compounds Production<sup>15</sup>*

The EDC/VCM process generates liquid residues (by-products) extracted from the EDC distillation train. These residues are a mixture of chlorinated hydrocarbons, comprising compounds heavier than EDC (such as chlorinated cyclic or aromatic compounds) and light compounds (C1 and C2 chlorinated hydrocarbons with lower boiling points than EDC).

Residues with a chlorine content of more than 60 % by weight can be recovered as follows:

- Feedstock for chlorinated solvents such as carbon tetrachloride / tetrachloroethylene;
- Gaseous hydrogen chloride for re-use in the oxychlorinator; or
- Marketable hydrochloric acid solution.

<sup>14</sup> EIPPCB BREF (2003)

<sup>15</sup> EIPPCB BREF (2003)

The main solid wastes from EDC/VCM plants are spent oxychlorination catalyst, direct chlorination residues, and coke. Generic wastes also arise from wastewater treatment sludge, tank / vessel sludge, and maintenance activities.

Recommended management measures include the following:

- Spent oxychlorination catalyst is removed either continuously (by the entrainment of fines in fluid bed reactors), or periodically (when replacing exhausted fixed bed reactors). Depending on the process, the catalyst is recovered in a dry form or wet form, after settling and/or filtration of wastewater. Limited or trace quantities of heavy chlorinated organics (e.g., dioxins) adsorb onto waste catalyst; the concentration of these contaminants should determine the disposal method (usually incineration or landfill);
- Direct chlorination residues are generally pure or mixed inorganic iron salts. In high temperature chlorination, residues are recovered with the organic heavy compounds as a suspended solid. In low temperature chlorination, residues are recovered with wastewater and need alkali precipitation prior to separation by settling or filtration, possibly with the spent oxychlorination catalyst;
- Coke is formed by the thermal cracking of EDC and contains residual chlorinated hydrocarbons, although it does not contain PCDD/F. Coke is removed from the VCM by filtration. It also generates from decoking of the cracking section; and
- Final purification of VCM may involve the neutralization of acidity using lime. This generates a spent lime waste to be disposed of.

## Noise

Typical sources of noise generation include large size rotating machines, such as compressors and turbines, pumps, electric motors, air coolers, fired heaters, flares and from emergency

depressurization. Guidance on noise control and minimization is provided in the **General EHS Guidelines**.

## 1.2 Occupational Health and Safety

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

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

The most significant occupational health and safety hazards occur during the operational phase of an LVOC facility and primarily include:

- Process safety
- Chemical hazards

Major hazards should be managed according to international regulations and best practices (e.g., OECD Recommendations<sup>16</sup>, EU Seveso II Directive<sup>17</sup> and USA EPA Risk Management Program Rule<sup>18</sup>).

<sup>16</sup> OECD, Guiding Principles for Chemical Accident Prevention, Preparedness and Response, Second Edition (2003)

<sup>17</sup> EU Council Directive 96/82/EC, so-called Seveso II Directive, extended by the Directive 2003/105/EC.

<sup>18</sup> EPA, 40 CFR Part 68, 1996 — Chemical accident prevention provisions

## Process Safety

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

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

## Fire and Explosions

The most significant safety impacts are related to the handling and storage of large volumes of flammable and highly flammable LVOC products (e.g., lower olefins, aromatics, MTBE, ethylene oxide, acrylic esters and acrylic acid) at high temperature and pressure, combustible gases, and process chemicals. Explosions and fires due to accidental release of products are the major recorded accidents in LVOC manufacturing facilities. These events may cause significant acute exposures to workers and, potentially, to surrounding communities, depending on the quantities and types of accidentally released hazardous, volatile and flammable chemicals.

The risk of explosion of the gas clouds should be minimized through the following measures:

- Early detection of the release through installation of leak detection units and other devices;
- Segregating process areas, storage areas, utility areas, and safe areas, and adopting of safety distances<sup>19</sup>.
- Removing potential ignition sources;
- Controlling operation and procedures and avoiding hazardous gas mixtures;
- Removing or diluting the release and limiting the area affected by the loss of containment; and
- Developing, implementing, and maintaining a specific Emergency Management Plan providing emergence measures to be implemented to protect both operators and local communities from potential toxic products releases.

Risks of fires and explosions are also related to oxidation reactions (e.g., propylene oxidation reaction) and product management. Reactors should be installed following appropriate design criteria should be used<sup>20</sup>, for instance to manage explosive mixture of product powders (e.g., terephthalic acid / dimethyl terephthalate) with air.

## Ethylene Oxide

Ethylene oxide is toxic and a human carcinogen and EO gas is flammable, even without being mixed with air, and can auto-decompose explosively. The chemical properties of EO require various techniques to prevent any type of losses. In particular EO/EG storage and loading design should prevent should avoid ingress of air or impurities likely to react dangerously with EO, prevent leaks, and include a vapor return system for EO loading to minimize the gaseous streams to be handled.

<sup>19</sup> These distances can be derived from safety analyses specific for the facility, considering the occurrence of the hazards or from applicable standards or guidelines (e.g., API, NFPA).

<sup>20</sup> NFPA 654: Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids

### Acrylic Esters

The propylene oxidation process is a hazardous step, primarily due to flammability, that must be managed carefully<sup>21</sup>. Storage and transportation of acrylic acid and esters should also be carefully designed and managed, due to explosion hazards associated to uncontrolled polymerization.<sup>22,23</sup>

Acrylic acid is inhibited with hydroquinone mono methyl ether, which is active in presence of air. It is easy flammable when overheated. It should be stored in stainless steel tanks, in contact with atmosphere of 5-21 percent oxygen, at temperature of 15 - 25 °C, avoiding overheating or freezing. Thawing of frozen acrylic acid can cause runaway polymerization; therefore, thawing should be conducted under controlled conditions using mild heating systems.

### Acrylonitrile and Hydrogen Cyanide<sup>24</sup>

Hazardous properties of these two compounds require specific safety considerations in their manufacturing, storage and handling. Due to its reactive and toxic nature, hydrogen cyanide cannot be stored for periods longer than a few days. If the material cannot be sold or used, it must be burnt. The capability to destroy all of the hydrogen cyanide produced should therefore be ensured. Acrylonitrile can self-polymerize if initiators are present, and is flammable. Stabilizing agents should therefore be added to the product, and measures taken to prevent the accidental ingress of impurities that could either strongly react or catalyze a runaway reaction.

### Nitrobenzene<sup>25</sup>

Nitrobenzene is a very toxic substance, and very toxic byproducts (e.g., nitrophenols and picric acid) are produced in the process. In areas of high vapor concentrations (>1 ppm), full face masks with organic-vapor canisters or air-supplied respirators should be used.

Fire and explosion hazards in nitrobenzene production are severe, related to the possibility of run-away nitration reaction<sup>26</sup> and to the explosivity of nitrogenated byproducts, like di- and tri nitrobenzene, nitrophenols and picric acid. Accurate design and control of nitration reactor should be ensured. During distillation and purification, high temperatures, high concentration of byproducts, and contamination from strong acids and bases and from corrosion products should be prevented to minimize risks of explosions<sup>27</sup>.

### Toluene Diisocyanate (TDI)<sup>28</sup>

Manufacturing of TDI involves a large number of hazardous substances, some in large quantities, such as chlorine, TDA, carbon monoxide, phosgene, hydrogen, nitric acid, nitrogen oxides, DNT, toluene, etc.

Contact with water and basic compounds such as caustic soda, amines, or other similar materials must be avoided, because their reaction with TDI causes the generation of heat and CO<sub>2</sub>. The liberation of CO<sub>2</sub> in tightly closed or restricted vessels or transfer lines may result in a violent rupture. Risk minimization measures include the following:

<sup>21</sup> J. R. Phimister, V. M. Bier, H. C. Kunreuther, Editors, National Academy of Engineering. Accident Precursor Analysis and Management: Reducing Technological Risk Through Diligence (2004)

<sup>22</sup> Acrylic acid - A summary of safety and handling, 3<sup>rd</sup> Edition (2002); Intercompany Committee for the Safety and Handling of Acrylic Monomers, ICESHAM

<sup>23</sup> Acrylate esters - A summary of safety and handling, 3<sup>rd</sup> Edition, 2002 ; Intercompany Committee for the Safety and Handling of Acrylic Monomers, ICESHAM

<sup>24</sup> EIPPCB BREF (2003)

<sup>25</sup> IPCS (International Programme on Chemical Safety), Environmental Health Criteria 230, Nitrobenzene. Available at <http://www.inchem.org/>

<sup>26</sup> R.V.C. Carr, Thermal hazards evaluation of aromatic nitration with nitric acid, Nitration Conference (1983)

<sup>27</sup> Japan Science and Technology Agency (JST), Failure knowledge database, Explosion at a nitrobenzene distillation column due to the lowering of reduced pressure from power failure. Available at <http://shippai.jst.go.jp/en/Search>

<sup>28</sup> EIPPCB BREF (2003)

- Store TDI in a dry environment using dry nitrogen or a dry air pad;
- Plug and cap all lines leading to and from storage tanks;
- Maintain and store all fittings and line connections in a dry environment;
- Avoid to tightly close any container of TDI that has been, or is suspected of having been, contaminated with water;
- Ensure that pure, washed DNT is not heated above 200 °C to avoid decomposition risks; and
- Very carefully handle phosgene, as follows:
  - Contain all phosgene operations in closed buildings;
  - Install phosgene sensors to monitor indoor concentrations;
  - If phosgene traces are detected, collect and treat all phosgene-contaminated indoor air (e.g., by alkaline scrubbing); and
  - Install an ammonia steam curtain system surrounding the phosgene unit. Ammonia is added to the steam to react with the phosgene in case of release. An alternative to this approach is building containment.

## Chemical Hazards

In case of LVOC releases, personnel can be exposed to concentrations dangerous for health and life. Toxic and carcinogenic compounds (e.g., aromatics, formaldehyde, ethylene oxide, acrylonitrile, hydrogen cyanide, nitrobenzene, toluene diisocyanate, vinyl chloride, 1,2 dichloroethane, carbon tetrachloride, and dioxin related components, predominantly the octo-chlorodibenzofuran generated in the oxychlorination reaction) are present in the process and stored on site.

The following measures should be implemented:

- Gas detectors should be installed in hazard areas, wherever possible;

- All spills should be avoided and precautions should be taken to control and minimize them;
- Adequate ventilation should be provided in all areas where hazardous and toxic products are handled; and
- Air extraction and filtration should be provided in all indoor areas where emissions and dust can be generated.

The potential for toxic releases in handling and storage of pressurized, refrigerated, and liquid hazardous products should be minimized adopting the following measures:

- Storage tanks should not be located close to installations where there is a risk of fire or explosion;
- Refrigerated storage is preferred for storage of large quantities of products, because the initial release in the case of a line or tank failure is slower than with pressurized storage systems;
- Alternative storage measures specifically applicable to liquid VCM include refrigerated storage and underground storage. Underground storage requires special tank design and environmental monitoring considerations to manage potential for soil and groundwater contamination.

Potential exposures to substances and chemicals during routine plant and maintenance operations should then 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**.

## 1.3 Community Health and Safety

The most significant community health and safety hazards associated with LVOC facilities occur during the operation phase and include the threat from major accidents related to potential fires and explosions in manufacturing processes or during product handling and transport outside the processing facility. Guidance for the management of these issues is

presented below and in relevant sections of the **General EHS Guidelines** including: Traffic Safety, Transport of Hazardous Materials, and Emergency Preparedness and Response.

The design of the facilities should include safeguards to minimize and control hazards to the community, through the following:

- Identifying reasonable design accident cases;
- Assessing the effects of the potential accidents on the surrounding areas;
- Properly selecting the plant location in respect to the local receptors, meteorological conditions (e.g., prevailing wind directions), and water resources (e.g., groundwater vulnerability) and identifying safe distances between the facilities and residential or commercial or other industrial areas;
- Identifying the prevention and mitigation measures required to avoid or minimize the hazards; and
- Providing information and involving the communities in emergency preparedness and response plans and relevant drills in case of major accident.

Community health and safety impacts during the decommissioning of LVOC manufacturing plants are common to those of most large industrial facilities, and are discussed in the **General EHS Guidelines**. These impacts include, among other things, transport safety, disposal of demolition waste that may include hazardous materials, and other impacts related to physical conditions and the presence of hazardous materials after site abandonment.

## 2.0 Performance Indicators and Monitoring

### 2.1 Environment

#### Emissions and Effluent Guidelines

Tables 1 and 2 present emission and effluent guidelines for this sector. Guideline values for process emissions and effluents in this sector are indicative of good international industry practice as reflected in relevant standards of countries with recognized regulatory frameworks. These guidelines are 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.

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

Effluent guidelines are applicable for direct discharges of treated effluents to surface waters for general use. Site-specific discharge levels may be established based on the availability and conditions in the 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**. These levels should be achieved, without dilution, at least 95 percent of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours. Deviation from these levels in consideration of

specific, local project conditions should be justified in the environmental assessment.

and individual projects should target continual improvement in these areas.

**Table 1. Air Emissions Guidelines<sup>a</sup>**

Pollutant	Unit	Guideline Value
Particulate Matter (PM)	mg/Nm <sup>3</sup>	20
Nitrogen Oxides	mg/Nm <sup>3</sup>	300
Hydrogen Chloride	mg/Nm <sup>3</sup>	10
Sulfur Oxides	mg/Nm <sup>3</sup>	100
Benzene	mg/Nm <sup>3</sup>	5
1,2-Dichloroethane	mg/Nm <sup>3</sup>	5
Vinyl Chloride (VCM)	mg/Nm <sup>3</sup>	5
Acrylonitrile	mg/Nm <sup>3</sup>	0.5 (incineration) 2 (scrubbing)
Ammonia	mg/Nm <sup>3</sup>	15
VOCs	mg/Nm <sup>3</sup>	20
Heavy Metals (total)	mg/Nm <sup>3</sup>	1.5
Mercury and Compounds	mg/Nm <sup>3</sup>	0.2
Formaldehyde	mg/m <sup>3</sup>	0.15
Ethylene	mg/Nm <sup>3</sup>	150
Ethylene Oxide	mg/m <sup>3</sup>	2
Hydrogen Cyanide	mg/m <sup>3</sup>	2
Hydrogen Sulfide	mg/m <sup>3</sup>	5
Nitrobenzene	mg/m <sup>3</sup>	5
Organic Sulfide and Mercaptans	mg/m <sup>3</sup>	2
Phenols, Cresols and Xylols (as Phenol)	mg/m <sup>3</sup>	10
Caprolactam	mg/m <sup>3</sup>	0.1
Dioxins/Furans	ng TEQ/Nm <sup>3</sup>	0.1

a. Dry, 273K (0°C), 101.3 kPa (1 atmosphere), 6% O<sub>2</sub> for solid fuels; 3% O<sub>2</sub> for liquid and gaseous fuels.

### Resource Use, Energy Consumption, Emission and Waste Generation

Table 3 provides examples of resource consumption indicators and energy for main products, whereas Table 4 provides examples of emission and waste generation indicators. Industry benchmark values are provided for comparative purposes only

**Table 2. Effluents Guidelines**

Pollutant	Unit	Guideline Value
pH	S.U.	6 - 9
Temperature Increase	°C	=3
BOD <sub>5</sub>	mg/l	25
COD	mg/l	150
Total Nitrogen	mg/l	10
Total Phosphorous	mg/l	2
Sulfide	mg/l	1
Oil and Grease	mg/l	10
TSS	mg/l	30
Cadmium	mg/l	0.1
Chromium (total)	mg/l	0.5
Chromium (hexavalent)	mg/l	0.1
Copper	mg/l	0.5
Zinc	mg/l	2
Lead	mg/l	0.5
Nickel	mg/l	0.5
Mercury	mg/l	0.01
Phenol	mg/l	0.5
Benzene	mg/l	0.05
Vinyl Chloride (VCM)	mg/l	0.05
1,2 Dichloroethane (EDC)	mg/l	1
Adsorbable Organic Halogens (AOX)	mg/l	1
Toxicity	Determined on a case specific basis	

### Environmental Monitoring

Environmental monitoring programs for this sector should be implemented to address all activities that have been identified to have potentially significant impacts on the environment, during normal operations and upset conditions. Environmental monitoring activities should be based on direct or indirect indicators of emissions, effluents, and resource use applicable to the particular project.

Monitoring frequency should be sufficient to provide representative data for the parameter being monitored. Monitoring should be conducted by trained individuals following monitoring and record-keeping procedures and using properly calibrated and maintained equipment. Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Additional guidance on applicable sampling and analytical methods for emissions and effluents is provided in the **General EHS Guidelines**.

**Table 3. Resource and Energy Consumption**

Product	Parameter	Unit	Industry Benchmark
Lower Olefins	Energy consumption Ethane feedstock	GJ/t ethylene	15-25
	Energy consumption Naphtha feedstock	GJ/t ethylene	25-40
	Energy consumption Gas oil feedstock	GJ/t ethylene	40-50
Aromatics	Steam	Kg/t feedstock	0.5-1
Formaldehyde Silver/Oxide process	Electricity	Kwh/t formaldehyde	100/200-225
VCM	Power	MWh/t VCM	1.2-1.3

Source: EIPPCB BREF (2003)

## 2.2 Occupational Health and Safety Performance

### Occupational Health and Safety Guidelines

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

**Table 4. Emissions, Effluents Waste/Co-Products Generation**

Product	Parameter	Unit	Industry Benchmark
Lower Olefins	Alkenes	t/y	2500
	CO, NOx	"	200
	SOx	"	600
	VOC	kg/t ethylene	0.6-10
	Waste Water Flow	m <sup>3</sup> /h	15
	Total hydroc. losses	% feed/ kg/t ethylene	0.3-0.5/5-15
Aromatics	NOx	kg/t feedstock	0-0.123
	SO <sub>2</sub>	kg/t feedstock	0-0.146
Acrylonitrile	Hydrogen cyanide	kg/t acrylonitrile	90-120
	Acetonitrile	kg/t acrylonitrile	5-32
	Ammonium sulfate	kg/t acrylonitrile	115-200
Caprolactam Basf/Rashig proc.	Ammonium sulfate	t/t caprolactam	2.5-4.5
TDI	COD/TOC	Kg/t TDI	6/2
	Nitrate, nitrite / sulfate	Kg/t TDI	15,10/24
VCM	Liquid residues	kg/t VCM	25-40
	Oxy catalyst	kg/t VCM	10-20
	Iron salts	kg/t VCM	10-50
	Coke	kg/t VCM	0.1-0.2

Source: EIPPCB BREF (2003)

Governmental Industrial Hygienists (ACGIH),<sup>29</sup> the Pocket Guide to Chemical Hazards published by the United States National Institute for Occupational Health and Safety (NIOSH),<sup>30</sup> Permissible Exposure Limits (PELs) published by the Occupational Safety and Health Administration of the United States (OSHA),<sup>31</sup> Indicative Occupational Exposure Limit Values published by European Union member states,<sup>32</sup> or other similar sources.

<sup>29</sup> <http://www.acgih.org/TLV/><sup>29</sup> Available at: <http://www.acgih.org/TLV/> and <http://www.acgih.org/store/>

<sup>30</sup> <sup>30</sup> Available at: <http://www.cdc.gov/niosh/npg/>

<sup>31</sup> <sup>31</sup> Available at: [http://www.osha.gov/pls/oshaweb/owadisp.show\\_document?p\\_table=STANDARDS&p\\_id=9992](http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=STANDARDS&p_id=9992)

<sup>32</sup> <sup>32</sup> Available at: [http://europe.osha.eu.int/good\\_practice/risks/ds/oe/](http://europe.osha.eu.int/good_practice/risks/ds/oe/)

## Accident and Fatality Rates

Projects should try to reduce the number of accidents among project workers (whether directly employed or subcontracted) to a rate of zero, especially accidents that could result in lost work time, different levels of disability, or even fatalities. Facility rates may be benchmarked against the performance of facilities in this sector in developed countries through consultation with published sources (e.g. US Bureau of Labor Statistics and UK Health and Safety Executive)<sup>33</sup>.

## Occupational Health and Safety Monitoring

The working environment should be monitored for occupational hazards relevant to the specific project. Monitoring should be designed and implemented by accredited professionals<sup>34</sup> 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**.

---

<sup>33</sup> Available at: <http://www.bls.gov/iif/> and <http://www.hse.gov.uk/statistics/index.htm>

<sup>34</sup> Accredited professionals may include Certified Industrial Hygienists, Registered Occupational Hygienists, or Certified Safety Professionals or their equivalent.

### 3.0 References and Additional Sources

- Carr, R.V.C. 1983. Thermal Hazards Evaluation of Aromatic Nitration with Nitric Acid. Nitration Conference, Menlo Park, California, 27-29 July 1983.
- European Commission. 2003. European Integrated Pollution Prevention and Control Bureau (EIPPCB) Reference Document on Best Available Techniques (BREF) for Large Volume Organic Chemicals. February 2003. Seville: EIPPCB. Available at <http://eippcb.jrc.es/pages/FActivities.htm>
- European Commission. 2000. Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the Incineration of Waste. Available at <http://europa.eu/scadplus/leg/en/lvb/l28072.htm>
- European Commission. 1996. Directive 96/82/EC on the control of chemical accidents (Seveso II) – Prevention, Preparedness and Response. Extended by Directive 2003/105/EC. Available at <http://ec.europa.eu/environment/seveso/index.htm>
- European Council of Vinyl Manufacturers (ECVM). 1994. Industry Charter for the Production of VCM and PVC (Suspension Process). Brussels: ECVM. Available at <http://www.ecvm.org/img/db/SPVCcharter.pdf>
- German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU). 2004. Waste Water Ordinance – AbwV. (Ordinance on Requirements for the Discharge of Waste Water into Waters). Promulgation of the New Version of the Waste Water Ordinance of 17 June 2004. Berlin: BMU. Available at [http://www.bmu.de/english/water\\_management/downloads/doc/3381.php](http://www.bmu.de/english/water_management/downloads/doc/3381.php)
- German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU). 2002. First General Administrative Regulation Pertaining the Federal Emission Control Act (Technical Instructions on Air Quality Control – TA Luft). Berlin: BMU. Available at [http://www.bmu.de/english/air\\_pollution\\_control/ta\\_luft/doc/36958.php](http://www.bmu.de/english/air_pollution_control/ta_luft/doc/36958.php)
- Intercompany Committee for the Safety and Handling of Acrylic Monomers (ICSHAM). 2002. Acrylate Esters – A Summary of Safety and Handling, 3rd Edition.
- Intergovernmental Panel on Climate Change (IPCC). 2006. IPCC Special Report on Carbon Dioxide Capture and Storage. Geneva: IPCC. Available at <http://www.ipcc.ch/activity/srccs/index.htm>
- International Programme on Chemical Safety (IPCS). Environmental Health Criteria 230. Nitrobenzene. Prepared by L. Davies. Joint Publication of United Nations Environment Programme (UNEP), International Labour Organization (ILO) and World Health Organization (WHO). Geneva: WHO. Available at <http://www.inchem.org/documents/ehc/ehc/ehc230.htm>
- Japan Science and Technology Agency (JST). Failure knowledge database. Available at <http://shippai.jst.go.jp/en/Search>
- Kirk-Othmer, R.E. 2006. Encyclopedia of Chemical Technology. 5th Edition. New York, NY: John Wiley and Sons Ltd.
- National Academy of Engineering. 2004. Eds. J.R. Phimister, V. M. Bier, H. C. Kunreuther. Accident Precursor Analysis and Management: Reducing Technological Risk Through Diligence. Washington, DC: National Academies Press.
- Organization for Economic Co-operation and Development (OECD). 2003. Guiding Principles for Chemical Accident Prevention, Preparedness and Response, Second Edition. Paris: OECD. Available at <http://www2.oecd.org/guidingprinciples/>
- Oslo and Paris Commission (OSPAR) for the Protection of the Marine Environment of the North Atlantic. OSPAR Decision 98/4 on Emission and Discharge Limit Values for the Manufacture of Vinyl Chloride Monomer (VCM) including the Manufacture of 1,2-dichloroethane (EDC). London: OSPAR. Available at [http://www.ospar.org/eng/html/dra/list\\_of\\_decrecs.htm#decisions](http://www.ospar.org/eng/html/dra/list_of_decrecs.htm#decisions)
- Ullmann's Encyclopedia of Industrial Chemistry, 2002. 6th edition. New York, NY: John Wiley and Sons Ltd. Available at <http://www.wiley-vch.de/vch/software/ullmann>
- United Kingdom (UK) Environmental Agency. 2003. Sector Guidance Note IPPC S4.01- Guidance for the Large Volume Organic Chemical Sector. Bristol: Environmental Agency. Available at <http://www.environment-agency.gov.uk/business/444304/1290036/1290086/1290209/1308462/1245952/?lang=e#>
- United Nations (UN). 2003. Recommendations on the Transport of Dangerous Goods. Model Regulations. Thirteenth revised edition. New York, NY: United Nations Publications. Available at <https://unp.un.org/>
- United States (US) Environment Protection Agency (EPA). 40 CFR Part 63 — National Emission Standards for Hazardous Air Pollutants, Subpart F—National Emission Standard for Vinyl Chloride. Washington, DC: US EPA. Available at <http://www.epa.gov/epacr40/chapt-I.info/>
- US EPA. 40 CFR Part 63 — National Emission Standards for Hazardous Air Pollutants, Subpart FFFF—National Emission Standards for Hazardous Air Pollutants: Miscellaneous Organic Chemical Manufacturing. Washington, DC: US EPA. Available at <http://www.epa.gov/epacr40/chapt-I.info/>
- US EPA. 40 CFR Part 68— Chemical accident prevention and provisions. Washington, DC: US EPA. Available at <http://www.epa.gov/epacr40/chapt-I.info/>
- US National Fire Protection Association (NFPA). 2006. NFPA 654: Standard for the Prevention of Fire and Dust Explosions from the Manufacturing, Processing, and Handling of Combustible Particulate Solids. Quincy, MA: NFPA. Available at <http://www.nfpa.org/aboutthecodes/AboutTheCodes>

## Annex A: General Description of Industry Activities

Large volume petroleum-based organic chemicals (LVOC) manufacturing represents the first step of the petrochemical industry. LVOC manufacturing transforms refinery products, through a combination of physical and chemical operations, into a variety of commodity or bulk chemicals, normally in continuously operated, integrated plants. LVOCs are used in large quantities as raw materials in the further synthesis of higher value chemicals (e.g. solvents, plastics, and drugs). Most LVOC manufacturing processes normally consist of raw material supply, synthesis, separation / refining, and handling / storage phases.

### Lower Olefins<sup>35</sup>

Lower olefins are the largest group of commodity chemicals within the LVOC manufacturing sector and are used for a wide range of derivatives. Feedstock range from light gases (e.g., ethane and LPGs) to refinery liquid products (e.g., naphtha, gas-oil). The use of heavier feedstock generally requires more complex plants and generates larger quantities of co-products (e.g., propylene, butadiene, benzene). The steam cracking route is the most common manufacturing process for both ethylene and propylene. Steam cracking is highly endothermic with the cracking reactions taking place in pyrolysis furnaces at temperatures above 800°C. Gas compression and cleanup with caustic soda and amines is conducted to remove acid gas and carbon dioxide. Recovery and purification of olefin products involves cryogenic separation. Ethylene is further purified to remove ethane by extractive distillation and acetylene by catalytic hydrogenation. Integrated plants allow for energy recovery. Operations directly associated with lower olefins manufacturing include feed pretreatment, butadiene recovery or hydrogenation, gasoline heat soaking or hydro-treatment,

benzene concentration or extraction, and tar handling. Olefin manufacturing plants require the capability to flare waste gases during an upset condition and certain intermittent operations. The highly volatile and flammable nature of the feedstock / products demands a high standard of safety, resulting in a low total hydrocarbon loss over the cracker.

### Aromatics<sup>36</sup>

Benzene, toluene, and xylenes (BTX) are produced from three main feedstocks, namely, refinery reformates, steam cracker pyrolysis gasoline (pygas), and benzene from coal tar processing. The separation of aromatics from non-aromatics and the isolation of pure products requires use of physical separation processes (e.g. azeotropic distillation, extractive distillation, liquid-liquid extraction, crystallization by freezing, adsorption, complexing with  $\text{BF}_3/\text{HF}$ ) and product chemical conversion (e.g. toluene to benzene by hydrodealkylation, to benzene and xylene by toluene disproportionation, and xylene and/or m-xylene to p-xylene by isomerization). Ethylbenzene can be separated by super-fractionation before xylene processing. Ethylbenzene is produced by alkylation of benzene with ethylene over an aluminum chloride or zeolite catalyst. Impurities such as methane, hydrogen, and ethane are usually combusted. The zeolite catalyst is regenerated using re-circulated nitrogen containing oxygen, and carbon dioxide is produced. Styrene is generally manufactured in a two-stage process comprising the catalytic alkylation of benzene with ethylene to produce ethylbenzene, followed by the catalytic dehydrogenation of ethylbenzene to produce styrene. The catalysts are usually an iron oxide base including chromium and potassium. Another commercial process consists of oxidation of ethylbenzene to ethylbenzene hydro-peroxide, followed by

<sup>35</sup> EIPPCB BREF (2003)

<sup>36</sup> Ibid.

reaction with propylene to give alpha phenyl ethanol and propylene oxide. The alcohol is then dehydrated to styrene. Crude liquid styrene, consisting primarily of styrene and ethylbenzene, is purified using low temperature vacuum distillation with sulfur or nitrogen-based inhibitors to minimize polymerization of vinyl-aromatic compounds.

In the two-stage cumene process, cumene is first formed by the alkylation of benzene and propylene over a fixed-bed of zeolites. Cumene is then oxidized to cumene hydroperoxide and then decomposed with an acid catalyst (usually sulfuric acid) to produce phenol, acetone and other co-products (e.g., acetophenone). Phenol and acetone are then purified by distillation. Two other processes to produce phenol are the toluene (Tolox) process (co-producing sodium benzoate) and the monochlorobenzene process. Emerging techniques for the production of phenol include vacuum pyrolysis of wood waste; reactive distillation in cumene production; and direct benzene oxidation.

## Oxygenated Compounds

Oxygenation compounds include a variety of LVOCs with diverse characteristics. The following are considered representative of this category: formaldehyde by methanol oxidation; MTBE (methyl t-butyl ether) from methanol and isobutene; ethylene oxide by ethylene oxidation; ethylene glycol by ethylene oxide hydration; terephthalic acid by oxidation of p-xylene; acrylic esters by propylene oxidation to acrolein and acrylic acid plus acrylic acid esterification.

### *Formaldehyde*<sup>37</sup>

Formaldehyde is produced from methanol by catalytic oxidation, either under air deficiency (silver process) or air excess (oxide process). The silver process is an oxidative dehydrogenation of

methanol with air over a crystalline silver catalyst. In the oxide process ('Formox') the formation of formaldehyde is obtained by direct oxidation of methanol with excess air over a metal oxide catalyst. The methanol oxidation is an exothermic reaction.

### *MTBE (Methyl Tert-Butyl Ether)*

MTBE is produced by the reaction of methanol with isobutene derived from various sources. Most commercially available processes are comparable and consist of a reaction and a refining section.

### *Ethylene Oxide / Ethylene Glycols*<sup>38</sup>

Ethylene oxide (EO) is a key chemical intermediate in the manufacture of many important products (e.g., ethylene glycols, ethoxylates, glycol ethers, and ethanol amines).

Ethylene oxide is produced from ethylene and oxygen in a gas phase reaction carried out in a multi-tubular, fixed bed type reactor, with a silver oxide catalyst in the tubes and a coolant on the shell side. Part of the ethylene feed is converted to CO<sub>2</sub> and water. Reaction products (EO, carbon dioxide, and water) are removed from the circulating gas while unconverted oxygen and ethylene are recycled back to the reactor. The recycle gas contains a diluent (e.g., methane), which allows operation at excess oxygen levels without causing a flammable mixture. EO is recovered by absorption in water followed by concentration in a stripper.

Ethylene glycols are produced by reacting EO with water at an elevated temperature (typically 150 - 250°C). The main product is Monoethylene Glycol (MEG) but valuable co-products are Diethylene Glycol (DEG) and Triethylene Glycol (TEG).

Ethylene oxide is toxic and a human carcinogen. Its gas can decompose explosively, even without being mixed with air or an

<sup>37</sup> EIPPCB BREF (2003)

<sup>38</sup> Ibid.

inert gas. The liquid phase polymerizes easily in the presence of alkalis, mineral acids, metal chlorides, metal oxides, iron, aluminum, or tin. These properties necessitate special arrangements for storage and handling.

### *Terephthalic Acid (TPA)*

Terephthalic acid is usually produced by liquid-phase air oxidation of p-xylene in the presence of soluble manganese and cobalt acetate catalysts and a sodium bromide promoter to form crude terephthalic acid. Acetic acid is the solvent, and oxygen in compressed air is the oxidant. Because of the highly corrosive bromine – acetic acid environment, the use of titanium-lined equipment is generally required. The crystalline crude terephthalic acid is collected as wet cake and dried. Solid terephthalic acid is then recovered by centrifugation or filtration, and the cake is dried and stored prior to purification ("crude terephthalic acid", >99 percent pure). The purification step involves dissolution in hot water under pressure and the catalytic selection of hydrogenating contaminants. The reaction is highly exothermic, and water is also released. The crude terephthalic acid is slurried with water and heated until it dissolves entirely. The TPA is then hydrogenated on a carbon-supported Pd catalyst in liquid phase. After reaction, TPA is crystallized, centrifuged and / or filtered, and then it is dried to a free flowing powder.

### *Dimethyl Terephthalate (DMT)*

Most dimethyl terephthalate (DMT) is made by a stepwise oxidation / esterification. P-xylene, together with recycled methyl p-toluate, is passed through an oxidation reactor along with catalyst, where p-toluic acid and monomethyl terephthalate are formed. It then passes to an esterification reactor, where the p-toluic acid and monomethyl terephthalate are converted noncatalytically to methyl p-toluate, returned to the oxidation

reactor, and DMT. An alternative process used to produce DMT is direct esterification of TPA.

### *Acrylic Esters*

Acrylic esters are a wide class of substances, ranging from methyl acrylate to hexadecyl acrylate. Acrylic esters are produced by esterification of acrylic acid, which in turn is produced by catalytic vapor phase oxidation of propylene with air or oxygen. Esterification plants are specialized to produce lower or higher esters, according to their boiling point (methyl to butyl esters vs. ethylhexyl to hexadecyl).

### **Nitrogenated Compounds**

Nitrogenated compounds include a large number of chemicals, and the following is focused on acrylonitrile; caprolactam; nitrobenzene; and toluene diisocyanate (TDI).

### *Acrylonitrile<sup>39</sup>*

Acrylonitrile is an intermediate monomer used world-wide for a number of applications. The BP/SOHIO process accounts for 95 percent of world-wide acrylonitrile capacity. The process is a vapor phase, exothermic ammoxidation of propylene in fluid bed reactors using excess ammonia in the presence of an air-fluidized catalyst bed. The process has three main co-products, namely hydrogen cyanide, acetonitrile, and ammonium sulfate. Catalyst is retained in the reactors using combinations of cyclones, although some is lost and exits the process through the quench system.

Water is produced in the reaction step and rejection of water from the process is a critical part of plant design. The concentrated, contaminated stream may be burnt or recycled to other parts of the process to maximize recovery of saleable products (before burning the contaminated stream). The

<sup>39</sup> EIPPCB BREF (2003)

reaction off-gases from the process absorber contains non-condensables (e.g., nitrogen, oxygen, carbon monoxide, carbon dioxide, propylene, propane) as well as vaporized water and traces of organic contaminants. An acrylonitrile plant may also have facilities to incinerate process residues and also to burn hydrogen cyanide.

### *Caprolactam*<sup>40</sup>

Caprolactam (hexamethylene imine) is the main raw material for the production of polyamide-6 (nylon). Caprolactam is mainly produced via the intermediate cyclohexanone (ketohexamethylene). A caprolactam production unit typically consists of four stages. (1) Cyclohexanone (ANON) plant where cyclohexanone is produced catalytically from phenol and hydrogen. By-products are cyclohexanol and residues (tar); (2) Hydroxylamine phosphate oxime (HPO) plant where oxime is produced via the phosphate route; (3) Hydroxylamine sulfate oxime (HSO) and caprolactam purification plant where oxime from the HSO route plus the oxime from the phosphate route are converted to caprolactam via the sulfate route; (4) Caprolactam finishing plant with caprolactam extraction with benzene and water wash removing ammonium sulfate and organic impurities.

### *Nitrobenzene*<sup>41</sup>

Mono-, di-, and symmetrical trinitrobenzenes are readily available by sequential nitration of benzene. A continuous process, operating under similar conditions, has replaced the traditional batch nitration process in which mixed acid (nitric and sulfuric acids) is added to a slight excess of benzene. The current production facilities are package units with nitrogen blanketing for additional safety. Each output stream passes through purging steps. Spent acid is extracted with incoming

benzene to remove both residual nitrobenzene and nitric acid, while residual waste gases are scrubbed by a mixed acid loop. An alternative process is pump nitration, where nitration actually takes place in the pump itself.

### *Toluene Diisocyanate (TDI)*<sup>42</sup>

Aromatic isocyanates are produced in highly integrated production sites and this typically includes integrated phosgene production. All TDI is manufactured from toluene by the phosgene route. This continuous process involves three steps. (1) Nitration of toluene where nitrating acid are formed. The used acid is purified and concentrated for re-use and the mixture of dinitrotoluenes is processed in an alkaline scrubber using water, or sodium carbonate solution and further fresh water, and further purified by crystallization; (2) Hydrogenation of dinitrotoluene to toluene diamine is a catalytic exothermic gas / liquid / solid phase reaction. Dinitrotoluene is reduced to toluene-diamine (TDA) by a continuous, one or multi-stage, hydrogenation process with metal catalysts. The reaction product is separated in a TDA-rich product stream, cleaned from the residual catalyst by filtration or centrifugation, followed by a distillation to recycle the solvent (if used); and (4) Phosgenation of toluene diamine to toluene diisocyanate which is an integrated route including the manufacture of phosgene. Toluene diisocyanate (TDI) is always produced by the reaction of phosgene with TDA in a cascade of reactors. TDI may be produced directly from dinitrotoluene by liquid phase carbonylation with *o*-dichlorobenzene.

<sup>40</sup> Ibid.

<sup>41</sup> Kirk-Othmer (2006) and Ullman (2002)

<sup>42</sup> EIPPCB BREF (2003)

## Halogenated Compounds<sup>43</sup>

### *Ethylene Dichloride (EDC) / Vinyl Chloride Monomer (VCM)*

The EDC / VCM process is often integrated with chlorine and ethylene production sites because of the issues related to chlorine and ethylene transportation and because this production chain is the largest single chlorine consumer. EDC (or 1, 2 dichloroethane) is synthesized by the chlorination of ethylene (direct chlorination) or by the chlorination of ethylene with HCl and oxygen (oxychlorination). Thermal cracking of dry, pure EDC produces VCM and HCl. By using both direct chlorination and oxychlorination for EDC, a high level of integration and by-product utilization is achieved in a balanced unit. In direct chlorination, EDC is synthesized by the exothermic reaction of ethylene and chlorine, catalyzed by metal chlorides.

In oxychlorination, EDC and water are formed by the gaseous phase reaction of HCl, ethylene and oxygen over a copper-salt catalyst either on fixed or fluidized-catalyst bed. The reaction is highly exothermic and temperature control is important to minimize the formation of undesirable by-products. HCl is normally recycled from the EDC cracking unit and from VCM purification. Use of air increases the formation of chlorinated by-products and produces larger waste gas streams, while oxygen significantly reduces by-products formation and volume of vented gases. Oxychlorination generates a number of waste streams including impurities (e.g., mono-chloroethane and 1,1,2 trichloroethane) as by-products from the EDC distillation section requiring treatment prior to emission to atmosphere; aqueous effluent from reactor outlet quenching, condensation and phase separation containing small quantities of dissolved chlorinated organic compounds (chloral or chloro-ethanol) and possibly copper (dissolved or as suspended matter) coming from fines catalyst fines (fluid bed reactors only); and spent catalyst on a

<sup>43</sup> Ibid.

periodic basis (fixed-bed reactors only). EDC purification, to eliminate impurities which can inhibit EDC cracking, may entail various steps including washing with water and caustic to remove traces of HCl, chlorine, entrained catalyst and some water-soluble organics; azeotropic drying / light ends distillation; heavy ends distillation; further light ends and heavy ends processing; and chlorination reaction. EDC cracking is achieved in heated furnaces at temperatures of approximately 500 °C, where EDC splits into VCM and HCl followed by quenching, normally with cold, recycled EDC condensate, to reduce tars and heavy by-products formation. EDC feed must be more than 99.5 percent pure to reduce coke formation and fouling of the pyrolysis reactor and dry to prevent equipment corrosion by hydrogen chloride. Coke build-up is periodically removed for disposal.

VCM purification is a two-stage distillation. Liquid VCM is stored after an optional step to remove the last traces of HCl. No gaseous emissions are generated in this section and there are only minor quantities of waste (e.g., spent hydrogenation catalyst, and spent alkaline agent for VCM neutralization). EDC / VCM production operations normally include large storage facilities. EDC and byproducts are stored in atmospheric tanks at ambient temperatures blanketed by nitrogen. VCM storage is in spheres or tanks that can either be under pressure at ambient temperature, or refrigerated at approximately atmospheric pressure. Liquefied dry HCl is generally in closed system pressurized vessels at low temperatures. Atmospheric storage vessels and products handling are the main source of gaseous vents in the form of breathing vents, vapor displacement during filling, and nitrogen blanketing.<sup>44</sup>

<sup>44</sup> Octo-chlorodibenzofuran and other dioxin related compounds are formed in the oxychlorination reactions as oxygen, chlorine and an organic precursor are all present at high temperatures in the presence of a catalyst. OSPAR data for two different plants showed a total formation of dioxins in the internal process of 6 g/year for a fluid bed and 40 g/year for a fixed bed reactor. However, these quantities are not emitted into the environment since further control measures are to be implemented.