EUROPEAN COMMISSION

Integrated Pollution Prevention and Control (IPPC)

Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry

February 2003

EXECUTIVE SUMMARY

The Large Volume Organic Chemicals (LVOC) BREF (Best Available Techniques reference document) reflects an information exchange carried out under Article 16(2) of Council Directive 96/61/EC. This Executive Summary - which is intended to be read in conjunction with both the standard introduction to the BAT chapters and the BREF Preface's explanations of objectives, usage and legal terms - describes the main findings, the principal BAT conclusions and the associated emission / consumption levels. It can be read and understood as a stand-alone document but, as a summary, it does not present all the complexities of the full BREF text. It is therefore not intended as a substitute for the full BREF text as a tool in BAT decision making.

Document scope and organisation: For the purposes of BAT information exchange the organic chemical industry has been divided into sectors for 'Large Volume Organic Chemicals', 'Polymers' and 'Fine Organic Chemicals'. The IPPC directive does not use the term 'Large Volume Organic Chemicals' and so offers no assistance in its definition. The TWG interpretation, however, is that it covers those activities in sections 4.1(a) to 4.1(g) of Annex 1 to the Directive with a production rate of more than 100 kt/yr. In Europe, some 90 organic chemicals meet these criteria. It has not been possible to carry out a detailed information exchange on every LVOC process because the scope of LVOC is so large. The BREF therefore contains a mixture of generic and detailed information on LVOC processes:

- *Generic information:* LVOC applied processes are described both in terms of widely used unit processes, unit operations and infrastructure (Chapter 2), and also using brief descriptions of the main LVOC processes (Chapter 3). Chapter 4 gives the generic origins, and possible composition, of LVOC emissions and Chapter 5 outlines the available emission prevention and control techniques. Chapter 6 concludes by identifying those techniques that are considered to be generic BAT for the LVOC sector as a whole.
- *Detailed information:* The LVOC industry has been divided into eight sub-sectors (based on functional chemistry) and, from these, 'illustrative processes' have been selected to demonstrate the application of BAT. The seven illustrative processes are characterised by major industrial importance, significant environmental issues and operation at a number of European sites. There are no illustrative processes for the LVOC sub-sectors covering sulphur, phosphorous and organo-metal compounds but for other sub-sectors they are:

Sub-sector	Illustrative process
Lower Olefins	Lower olefins (by the cracking process) - Chapter 7
Aromatics	Benzene / toluene / xylene (BTX) aromatics – Chapter 8
Oxygenated compounds	Ethylene oxide & ethylene glycols – Chapter 9 Formaldehyde – Chapter 10
Nitrogenated compounds	Acrylonitrile – Chapter 11 Toluene diisocyanate – Chapter 13
Halogenated compounds	Ethylene dichloride (EDC) & Vinyl Chloride Monomer (VCM) – Chapter 12

Valuable information on LVOC processes is also to be found in other BREFs. Of particular importance are the 'horizontal BREFs' (especially Common waste water and waste gas treatment/management systems in the chemical industry, Storage and Industrial cooling systems) and vertical BREFs for related processes (especially Large Combustion Plants).

Background information (Chapter 1)

LVOC encompasses a large range of chemicals and processes. In very simplified terms it can be described as taking refinery products and transforming them, by a complex combination of physical and chemical operations, into a variety of 'commodity' or 'bulk' chemicals; normally in continuously operated plants. LVOC products are usually sold on chemical specifications rather than brand name, as they are rarely consumer products in their own right. LVOC products are more commonly used in large quantities as raw materials in the further synthesis of higher value chemicals (e.g. solvents, plastics, drugs).

LVOC processes are usually located on large, highly integrated production installations that confer advantages of process flexibility, energy optimisation, by-product re-use and economies of scale. European production figures are dominated by a relatively small number of chemicals manufactured by large companies. Germany is Europe's largest producer but there are well-established LVOC industries in the Netherlands, France, the UK, Italy, Spain and Belgium.

LVOC production has significant economic importance in Europe. In 1995 the European Union was an exporter of basic chemicals, with the USA and EFTA countries being the main recipients. The market for bulk chemicals is very competitive, with cost of production playing a very large part, and market share is often considered in global terms. The profitability of the European LVOC industry is traditionally very cyclical. This is accentuated by high capital investment costs and long lead-times for installing new technology. As a result, reductions in manufacturing costs tend to be incremental and many installations are relatively old. The LVOC industry is also highly energy intensive and profitability is often linked to oil prices.

The 1990s saw a stronger demand for products and a tendency for major chemical companies to create strategic alliances and joint ventures. This has rationalised research, production and access to markets, and increased profitability. Employment in the chemicals sector continues to decline and dropped by 23 % in the ten-year period from 1985 to 1995. In 1998, a total of 1.6 million staff were employed in the EU chemicals sector.

Generic LVOC production process (Chapter 2)
Although processes for the production of LVOC are extremely diverse and complex, they are typically composed of a combination of simpler activities and equipment that are based on similar scientific and engineering principles. Chapter 2 describes how unit processes, unit operations, site infrastructure, energy control and management systems are combined and modified to create a production sequence for the desired LVOC product. Most LVOC processes can be described in terms of five distinct steps, namely: raw material supply / work-up, synthesis, product separation / refining, product handling / storage, and emission abatement.

Generic applied processes and techniques (Chapter 3)
Since the vast majority of LVOC production processes have not benefited from a detailed information exchange, Chapter 3 provides very brief ('thumbnail') descriptions of some 65 important LVOC processes. The descriptions are restricted to a brief outline of the process, any significant emissions, and particular techniques for pollution prevention / control. Since the descriptions aim to give an initial overview of the process, they do not necessarily describe all production routes and further information may be necessary to reach a BAT decision.

Generic emissions from LVOC processes (Chapter 4)
Consumption and emission levels are very specific to each process and are difficult to define and quantify without detailed study. Such studies have been undertaken for the illustrative processes but, for other LVOC processes, Chapter 4 gives generic pointers to possible pollutants and their origins. The most important causes of process emissions are[InfoMil, 2000 #83]:

- contaminants in raw materials may pass through the process unchanged and exit as wastes
- the process may use air as an oxidant and this creates a waste gas that requires venting
- process reactions may yield water / other by-products requiring separation from the product
- auxiliary agents may be introduced into the process and not fully recovered
- there may be unreacted feedstock which cannot be economically recovered or re-used.

The exact character and scale of emissions will depend on such factors as: plant age; raw material composition; product range; nature of intermediates; use of auxiliary materials; process conditions; extent of in-process emission prevention; end-of-pipe treatment technique; and the operating scenario (i.e. routine, non-routine, emergency). It is also important to understand the actual environmental significance of such factors as: plant boundary definition; the degree of process integration; definition of emission basis; measurement techniques; definition of waste; and plant location.

Generic techniques to consider in the determination of BAT (Chapter 5)

Chapter 5 provides an overview of generic techniques for the prevention and control of LVOC process emissions. Many of the techniques are also described in relevant horizontal BREFs. LVOC processes usually achieve environmental protection by using a combination of techniques for process development, process design, plant design, process-integrated techniques and end-of-pipe techniques. Chapter 5 describes these techniques in terms of management systems, pollution prevention and pollution control (for air, water and waste).

Management systems. Management systems are identified as having a central role in minimising the environmental impact of LVOC processes. The best environmental performance is usually achieved by the installation of the best technology and its operation in the most effective and efficient manner. There is no definitive Environmental Management System (EMS) but they are strongest where they form an inherent part of the management and operation of a LVOC process. An EMS typically addresses the organisational structure, responsibilities, practices, procedures, processes and resources for developing, implementing, achieving, reviewing and monitoring the environmental policy[InfoMil, 2000 #83].

Pollution prevention. IPPC presumes the use of preventative techniques before any consideration of end-of-pipe control techniques. Many pollution prevention techniques can be applied to LVOC processes and Section 5.2 describes them in terms of source reduction (preventing waste arisings by modifications to products, input materials, equipment and procedures), recycling and waste minimisation initiatives.

Air pollutant control. The main air pollutants from LVOC processes are Volatile Organic Compounds (VOCs) but emissions of combustion gases, acid gases and particulate matter may also be significant. Waste gas treatment units are specifically designed for a certain waste gas composition and may not provide treatment for all pollutants. Special attention is paid to the release of toxic / hazardous components. Section 5.3 describes techniques for the control of generic groups of air pollutants.

Volatile Organic Compounds (VOCs). VOCs typically arise from process vents, the storage / transfer of liquids and gases, fugitive sources and intermittent vents. The effectiveness and costs of VOC prevention and control will depend on the VOC species, concentration, flow rate, source and target emission level. Resources are typically targeted at high flow, high concentration, process vents but recognition must be given to the cumulative impact of low concentration diffuse arisings, especially as point sources become increasingly controlled.

VOCs from process vents are, where possible, re-used within processes but this is dependent on such factors as VOC composition, any restrictions on re-use and VOC value. The next alternative is to recover the VOC calorific content as fuel and, if not, there may be a requirement for abatement. A combination of techniques may be needed, for example: pre-treatment (to remove moisture and particulates); concentration of a dilute gas stream; primary removal to reduce high concentrations, and finally polishing to achieve the desired release levels. In general terms, condensation, absorption and adsorption offer opportunities for VOC capture and recovery, whilst oxidation techniques involve VOC destruction.

VOCs from fugitive emissions are caused by vapour leaks from equipment as a result of gradual loss of the intended tightness. The generic sources may be stem packing on valves / control valves, flanges / connections, open ends, safety valves, pump / compressor seals, equipment manholes and sampling points. Although the fugitive loss rates from individual pieces of equipment are usually small, there are so many pieces on a typical LVOC plant that the total loss of VOCs may be very significant. In many cases, using better quality equipment can result in significant reductions in fugitive emissions. This does not generally increase investment costs on new plants but may be significant on existing plants, and so control relies more heavily on Leak Detection and Repair (LDAR) programmes. General factors that apply to all equipment are:

- minimising the number of valves, control valves and flanges, consistent with plant safe operability and maintenance needs.
- improving access to potential leaking components to enable effective maintenance.
- leaking losses are hard to determine and a monitoring programme is a good starting point to gain insight into the emissions and the causes. This can be the basis of an action plan
- the successful abatement of leaking losses depends heavily on both technical improvements and the managerial aspects since motivation of personnel is an important factor
- abatement programmes can reduce the unabated losses (as calculated by average US-EPA emission factors) by 80 - 95 %
- special attention should be paid to long term achievements
- most reported fugitive emissions are calculated rather than monitored and not all calculation formats are comparable. Average emissions factors are generally higher than measured values.

Combustion units (process furnaces, steam boilers and gas turbines) give rise to emissions of carbon dioxide, nitrogen oxides, sulphur dioxide and particulates. Nitrogen oxide emissions are most commonly reduced by combustion modifications that reduce temperatures and hence the formation of thermal NOx. The techniques include low NOx burners, flue gas recirculation, and reduced pre-heat. Nitrogen oxides can also be removed after they have formed by reduction to nitrogen using Selective Non Catalytic Reduction (SNCR) or Selective Catalytic Reduction (SCR).

Water pollutant control. The main water pollutants from LVOC processes are mixtures of oil / organics, biodegradable organics, recalcitrant organics, volatile organics, heavy metals, acid / alkaline effluents, suspended solids and heat. In existing plants, the choice of control techniques may be restricted to process-integrated (in-plant) control measures, in-plant treatment of segregated individual streams and end-of-pipe treatment. New plants may provide better opportunities to improve environmental performance through the use of alternative technologies to prevent waste water arisings.

Most waste water components of LVOC processes are biodegradable and are often biologically treated at centralised waste water treatment plants. This is dependent on first treating or recovering any waste water streams containing heavy metals or toxic or non-biodegradable organic compounds using, for example, (chemical) oxidation, adsorption, filtration, extraction, (steam) stripping, hydrolysis (to improve bio-degradability) or anaerobic pre-treatment.

Waste control. Wastes are very process-specific but the key pollutants can be derived from knowledge of: the process, construction materials, corrosion / erosion mechanisms and maintenance materials. Waste audits are used to gather information on the source, composition, quantity and variability of all wastes. Waste prevention typically involves preventing the arising of waste at source, minimising the arisings and recycling any waste that is generated. The choice of treatment technique is very specific to the process and the type of waste arisings and is often contracted-out to specialised companies. Catalysts are often based on expensive metals and are regenerated. At the end of their life the metals are recovered and the inert support is landfilled. Purification media (e.g. activated carbon, molecular sieves, filter media, desiccants and ion exchange resins) are regenerated where possible but landfill disposal and incineration (under appropriate conditions) may also be used. The heavy organic residues from distillation columns and vessel sludges etc. may be used as feedstock for other processes, or as a fuel (to capture the calorific value) or incinerated (under appropriate conditions). Spent reagents (e.g. organic solvents), that cannot be recovered or used as a fuel, are normally incinerated (under appropriate conditions).

Heat emissions may be reduced by 'hardware' techniques (e.g. combined heat and power, process adaptations, heat exchange, thermal insulation). Management systems (e.g. attribution of energy costs to process units, internal reporting of energy use/efficiency, external benchmarking, energy audits) are used to identify the areas where hardware is best employed.

Techniques to reduce _vibrations_ include: selection of equipment with inherently low vibration, anti-vibration mountings, the disconnection of vibration sources and surroundings and consideration at the design stage of proximity to potential receptors.

Noise may arise from such equipment as compressors, pumps, flares and steam vents. Techniques include: noise prevention by suitable construction, sound absorbers, noise control booth / encapsulation of the noise sources, noise-reducing layout of buildings, and consideration at the design stage of proximity to potential receptors.

A number of _evaluation tools_ may be used to select the most appropriate emission prevention and control techniques for LVOC processes. Such evaluation tools include risk analysis and dispersion models, chain analysis methods, planning instruments, economic analysis methods and environmental weighting methods.

Generic BAT (Chapter 6)

The component parts of Generic BAT are described in terms of management systems, pollution prevention / minimisation, air pollutant control, water pollutant control and wastes / residues control. Generic BAT applies to the LVOC sector as a whole, regardless of the process or product. BAT for a particular LVOC process is, however, determined by considering the three levels of BAT in the following order of precedence:

1. illustrative process BAT (where it exists)
2. LVOC Generic BAT; and finally
3. any relevant Horizontal BAT (especially from the BREFs on waste water / waste gas management and treatment, storage and handling, industrial cooling, and monitoring).

Management systems: Effective and efficient management systems are very important in the attainment of high environmental performance. BAT for environmental management systems is an appropriate combination or selection of, *inter alia*, the following techniques:

- an environmental strategy and a commitment to follow the strategy
- organisational structures to integrate environmental issues into decision-making
- written procedures or practices for all environmentally important aspects of plant design, operation, maintenance, commissioning and decommissioning
- internal audit systems to review the implementation of environmental policies and to verify compliance with procedures, standards and legal requirements
- accounting practices that internalise the full costs of raw materials and wastes
- long term financial and technical planning for environmental investments
- control systems (hardware / software) for the core process and pollution control equipment to ensure stable operation, high yield and good environmental performance under all operational modes
- systems to ensure operator environmental awareness and training
- inspection and maintenance strategies to optimise process performance
- defined response procedures to abnormal events
- ongoing waste minimisation exercises.

Pollution prevention and minimisation: The selection of BAT for LVOC processes, for all media, is to give sequential consideration to techniques according to the hierarchy:

a) eliminate arisings of all waste streams (gaseous, aqueous and solid) through process development and design, in particular by high-selectivity reaction step and proper catalyst
b) reduce waste streams at source through process-integrated changes to raw materials, equipment and operating procedures
c) recycle waste streams by direct re-use or reclamation / re-use
d) recover any resource value from waste streams
e) treat and dispose of waste streams using end-of-pipe techniques.

BAT for the design of new LVOC processes, and for the major modification of existing processes, is an appropriate combination or selection of the following techniques:

- carry out chemical reactions and separation processes continuously, in closed equipment
- subject continuous purge streams from process vessels to the hierarchy of: re-use, recovery, combustion in air pollution control equipment, and combustion in non-dedicated equipment
- minimise energy use and to maximise energy recovery
- use compounds with low or lower vapour pressure
- give consideration to the principles of 'Green Chemistry'.

BAT for the prevention and control of **fugitive emissions** is an appropriate combination or selection of, *inter alia*, the following techniques:

- a formal Leak Detection and Repair (LDAR) programme to focus on the pipe and equipment leak points that provide the highest emission reduction per unit expenditure
- repair pipe and equipment leaks in stages, carrying out immediate minor repairs (unless this is impossible) on points leaking above some lower threshold and, if leaking above some higher threshold, implement timely intensive repair. The exact threshold leak rate at which repairs are performed will depend on the plant situation and the type of repair required.
- replace existing equipment with higher performance equipment for large leaks that cannot otherwise be controlled
- install new facilities built to tight specifications for fugitive emissions
- the following, or equally efficient, high performance equipment:
    - **valves**: low leak rate valves with double packing seals. Bellow seals for high-risk duty
    - **pumps**: double seals with liquid or gas barrier, or seal-less pumps
    - **compressors and vacuum pumps**: double seals with liquid or gas barrier, or seal-less pumps, or single seal technology with equivalent emission levels
    - **flanges**: minimise the number, use effective gaskets
    - **open ends**: fit blind flanges, caps or plugs to infrequently used fittings; use closed loop flush on liquid sampling points; and, for sampling systems / analysers, optimise the sampling volume/frequency, minimise the length of sampling lines or fit enclosures.
    - **safety valves**: fit upstream rupture disk (within any safety limitations).

BAT for **storage, handling and transfer** is, in addition to those in the Storage BREF, an appropriate combination or selection of, *inter alia*, the following techniques:

- external floating roof with secondary seals (not for highly dangerous substances), fixed roof tanks with internal floating covers and rim seals (for more volatile liquids), fixed roof tanks with inert gas blanket, pressurised storage (for highly dangerous or odorous substances)
- inter-connect storage vessels and mobile containers with balance lines
- minimise the storage temperature
- instrumentation and procedures to prevent overfilling
- impermeable secondary containment with a capacity of 110 % of the largest tank
- recover VOCs from vents (by condensation, absorption or adsorption) before recycling or destruction by combustion in an energy raising unit, incinerator or flare
- continuous monitoring of liquid level and changes in liquid level
- tank filling pipes that extend beneath the liquid surface
- bottom loading to avoid splashing
- sensing devices on loading arms to detect undue movement
- self-sealing hose connections / dry break coupling
- barriers and interlock systems to prevent accidental movement or drive-away of vehicles.

BAT for preventing and minimising the emission of **water pollutants** is an appropriate combination or selection of the following techniques:

A. identify all waste water arisings and characterise their quality, quantity and variability
B. minimise water input to the process
C. minimise process water contamination with raw material, product or wastes
D. maximise waste water re-use
E. maximise the recovery / retention of substances from mother liquors unfit for re-use.

BAT for **energy efficiency** is an appropriate combination or selection of the following techniques: optimise energy conservation; implement accounting systems; undertake frequent energy reviews; optimise heat integration; minimise the need for cooling systems; and adopt Combined Heat and Power systems where economically and technically viable.

BAT for the prevention and minimisation of **noise and vibration** is an appropriate combination or selection of the following techniques:

- adopt designs that disconnect noise / vibration sources from receptors
- select equipment with inherently low noise / vibration levels; use anti-vibration mountings; use sound absorbers or encapsulation
- periodic noise and vibration surveys.

Air pollutant control: The BAT selection requires consideration of parameters such as: pollutant types and inlet concentrations; gas flow rate; presence of impurities; permissible exhaust concentration; safety; investment & operating cost; plant layout; and availability of utilities. A combination of techniques may be necessary for high inlet concentrations or less efficient techniques. Generic BAT for air pollutants is an appropriate combination or selection of the techniques given in Table A (for VOCs) and Table B (for other process related air pollutants).

Technique	BAT-associated values (1)	Remark
Selective membrane separation	90 - >99.9 % recovery VOC < 20 mg/m³	Indicative application range 1 - >10g VOC/m³ Efficiency may be adversely affected by, for example, corrosive products, dusty gas or gas close to its dew point.
Condensation	Condensation: 50 - 98 % recovery + additional abatement. Cryo-condensation: (2) 95 – 99.95 % recovery	Indicative application range: flow 100 - >100000 m³/h, 50 - >100g VOC/m³. For cryo-condensation: flow 10 – 1000 m³/h, 200 – 1000 g VOC/m³, 20 mbar-6 bar
Adsorption (2)	95 – 99.99 % recovery	Indicative application range for regenerative adsorption: flow 100 - >100000 m³/h, 0.01 - 10g VOC/m³, 1 – 20 atm. Non regenerative adsorption: flow 10 - >1000 m³/h, 0.01 - 1.2g VOC/m³
Scrubber (2)	95 - 99.9 % reduction	Indicative application range: flow 10 – 50000 m³/h, 0.3 - >5g VOC/m³
Thermal incineration	95 – 99.9 % reduction VOC (2) < 1 - 20 mg/m³	Indicative application range: flow 1000 – 100000m³/h, 0.2 - >10g VOC/m³. Range of 1 - 20 mg/m³ is based on emission limits & measured values. The reduction efficiency of regenerative or recuperative thermal incinerators may be lower than 95 – 99 % but can achieve < 20 mg/Nm³.
Catalytic oxidation	95 - 99 % reduction VOC < 1 - 20 mg/m³	Indicative application range: flow 10 – 100000 m³/h, 0.05 – 3 g VOC/m³
Flaring	Elevated flares > 99 % Ground flares > 99.5 %	
1. Unless stated, concentrations relate to half hour / daily averages for reference conditions of dry exhaust gas at 0 °C, 101.3 kPa and an oxygen content of 3 vol% (11 vol%. oxygen content in the case of catalytic / thermal oxidation). 2. The technique has cross-media issues that require consideration.		

Table A: BAT-associated values for the recovery / abatement of VOCs

Pollutant	Technique	BAT-associated values (1)	Remark
Particulates	**Cyclone**	Up to 95 % reduction	Strongly dependent on the particle size. Normally only BAT in combination with another technique (e.g. electrostatic precipitator, fabric filter).
	Electrostatic precipitator	5 – 15 mg/Nm^3 99 – 99.9 % reduction	Based on use of the technique in different (non-LVOC) industrial sectors. Performance of is very dependent on particle properties.
	Fabric Filter	< 5 mg/Nm^3	
	Two stage dust filter	~ 1 mg/Nm^3	
	Ceramic filter	< 1 mg/Nm^3	
	Absolute Filter	< 0.1 mg/Nm^3	
	HEAF Filter	Droplets & aerosols up to 99 % reduction	
	Mist Filter	Dust & aerosols up to 99 % reduction	
Odour	**Adsorption** **Biofilter**	95 - 99 % reduction for odour and some VOC	Indicative application range: 10000 - 200000 ou/Nm^3
Sulphur dioxide & acid gases	**Wet limestone scrubbing**	90 – 97 % reduction SO_2 < 50 mg/Nm^3	Indicative range of application for SO_2 < 1000 mg/m^3 in the raw gas.
	Scrubbers	HCl (2) < 10 mg/Nm^3 HBr (2) < 5 mg/Nm^3	Concentrations based on Austrian permit limits.
	Semi Dry Sorbent Injection	SO_2 < 100 mg/Nm^3 HCl < 10 - 20 mg/Nm^3 HF < 1 - 5 mg/Nm^3	Indicative range of application for SO_2 < 1000 mg/m^3 in the raw gas.
Nitrogen oxides	**SNCR**	50 – 80 % NO_x reduction	
	SCR	85 to 95 % reduction NO_x <50 mg/m^3. Ammonia <5 mg/m^3	May be higher where the waste gas contains a high hydrogen concentration.
Dioxins	**Primary measures + adsorption** **3-bed catalyst**	< 0.1 ng TEQ/Nm^3	Generation of dioxins in the processes should be avoided as far as possible
Mercury	**Adsorption**	0.05 mg/Nm^3	0.01 mg/Nm^3 measured at Austrian waste incineration plant with activated carbon filter.
Ammonia & amines	**Scrubber**	<1 – 10 mgNm^3	Acid scrubber
Hydrogen sulphide	**Absorption (alkaline scrubber)**	1 - 5 mg/Nm^3	Absorption of H_2S is 99 %+. An alternative is absorption in an ethanolamine scrubber followed by sulphur recovery.

1. Unless stated, concentrations relate to half hour / daily averages for reference conditions of dry exhaust gas at 0 °C, 101.3 kPa and an oxygen content of 3 vol%.
2. Daily mean value at standard conditions. The half hourly values are HCl <30 mg/m^3 and HBr <10 mg/m^3.

Table B: BAT-associated values for the abatement of other LVOC air pollutants

Air pollutants emitted from LVOC processes have widely different characteristics (in terms of toxicity, global warming, photochemical ozone creation, stratospheric ozone depletion etc.) and are classified using a variety of systems. In the absence of a pan-European classification system, Table C presents BAT-associated levels using the Dutch NeR system. The NeR is consistent with a high level of environmental protection but is just one example of good practice. There are other, equally valid, classification systems that can be used to establish BAT-associated levels, some of which are outlined in Annex VIII of the BREF.

Categories **	Possible BAT solutions (not an exhaustive list)	BAT-associated emission level (mg/Nm^3) ***	Threshold (kg/h)
Extremely hazardous substances			
Dioxins & furans	Process integrated: good operating conditions and low chlorine in feedstock/fuel. End of pipe: Activated carbon, catalytic fabric filter, incinerator.	0.1 (ng I-TEQ/Nm^3)	no threshold
PCB's		0.1**** (ng PCB -TEQ/Nm^3)	no threshold
Particulates			
Particulate matter	If filtration is not possible, up to 25 applies If filtration is not possible, up to 50 applies	10 – 25 10 - 50	≥ 0.5 < 0.5
Carcinogenic substances*			
Σ C1	Incinerator, scrubber, absolute filter, activated carbon.	0.1	0.0005
Σ C1 + C2		1.0	0.005
Σ C1 + C2 + C3		5.0	0.025
Organic substances (gas/vapour)*			
Σ gO1	Incinerator, (regenerative) activated carbon, vapour recovery unit.	20	0.1
Σ gO1 + gO2		100	2.0
Σ gO1+ gO2 + gO3		100 - 150	3.0
Organic substances (solid)*			
Σ sO1	If filtration is not possible, up to 25 applies If filtration is not possible, up to 50 applies	10 – 25 10 - 50	≥ 0.1 < 0.1
Σ sO1 + sO2	If filtration is not possible, up to 25 applies If filtration is not possible, up to 50 applies	10 – 25 10 - 50	≥ 0.5 < 0.5
Σ sO1 + sO2 + sO3	If filtration is not possible, up to 25 applies If filtration is not possible, up to 50 applies	10 – 25 10 - 50	≥ 0.5 < 0.5
Inorganic substances (gas/vapour)			
gI1	Many different solutions (e.g. chemical scrubber, alkaline scrubber, activated carbon)	1.0	0.01
gI2		5.0	0.05
gI3		30	0.3
gI4	Acid/alkaline scrubber, S(N)CR, lime injection.	200	5
Inorganic substances (solid)*			
Σ sI1	Fabric filter, Scrubber, Electrostatic precipitator	0.2	0.001
Σ sI1 + sI2		1.0	0.005
Σ sI1 + sI2 + sI3		5.0	0.025

* The summation rule applies (i.e. the given emission level applies to the sum of the substances in the relevant category plus those of the lower category).

** Detailed substance classification is given in Annex VIII: Member State air pollutant classification systems.

*** The emission level only applies when the mass threshold (of untreated emissions) is exceeded. Emission levels relate to half hourly averages at normal conditions (dry exhaust gas, 0°C and 101.3 kPa). Oxygen concentration is not defined in the NeR but is usually the actual oxygen concentration (for incinerators 11 vol% oxygen may be acceptable).

**** Levels for PCBs are given here in terms of TEQ, for the relevant factors to calculate these levels, see article "Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife". "Van den Berg et al. Environmental Health Perspectives, Volume 106, No 12, December 1998"

Table C: Air emission levels associated with BAT for process vents in the LVOC industry

BAT for **flaring** is an appropriate combination or selection of, *inter alia*: plant design / operation to minimise the need for hydrocarbon disposal to the flare system. The choice between ground flares and elevated flares is based on safety. Where elevated flares are used, BAT includes permanent pilots / pilot flame detection, efficient mixing and remote monitoring by Closed Circuit Television. The BAT-associated reduction values for VOC are >99% for elevated flares and >99.5% for ground flares.

BAT for **process furnaces** is gas firing and low-NOx burner configuration to achieve associated emissions of 50 - 100 mg NOx /Nm^3 (as an hourly average) for new and existing situations. The BAT for **other combustion units** (e.g. steam boilers, gas turbines) can be found in the BREF on Large Combustion Plant.

BAT for **carbon dioxide emissions** is improved energy efficiency, but a switch to low-carbon (hydrogen-rich) fuels or sustainable non-fossil fuels may also be considered BAT.

Water pollutant control: BAT for water pollutants is an appropriate combination or selection of, *inter alia*, the following techniques:

- separate treatment or recovery of waste water streams containing heavy metals or toxic or non-biodegradable organic compounds using (chemical) oxidation, adsorption, filtration, extraction, (steam) stripping, hydrolysis or anaerobic pre-treatment, and subsequent biological treatment. The BAT-associated emission values in individual treated waste streams are (as daily averages): Hg 0.05 mg/l; Cd 0.2 mg/l; Cu / Cr / Ni / Pb 0.5 mg/l; and Zn / Sn 2 mg/l.
- organic waste water streams not containing heavy metals or toxic or non-biodegradable organic compounds are potentially fit for combined biological treatment in a lowly loaded plant (subject to evaluation of biodegradability, inhibitory effects, sludge deterioration effects, volatility and residual pollutant levels). The BAT-associated BOD level in the effluent is less than 20 mg/l (as a daily average).

LVOC process waste waters are strongly influenced by, *inter alia*, the applied processes, operational process variability, water consumption, source control measures and the extent of pre-treatment. But on the basis of TWG expert judgement, the BAT-associated emission levels (as daily averages) are: COD 30 – 125 mg/l; AOX < 1 mg/l; and total nitrogen 10 - 25 mg/l.

Wastes and residues control: BAT for wastes and residues is an appropriate combination or selection of, *inter alia*, the following techniques:

- catalysts - regeneration / re-use and, when spent, to recover the precious metal content
- spent purification media - regeneration where possible, and if not to landfill or incinerate
- organic process residues - maximise use as feedstock or as fuel, and if not to incinerate
- spent reagents - maximise recovery or use as fuel, and if not to incinerate.

Illustrative process: Lower Olefins (Chapter 7)

General information: Lower Olefins encompasses the largest group of commodity chemicals within the LVOC sector and are used for a very wide range of derivatives. In 1998, European ethylene production was 20.3 million tonnes and propylene production was 13.6 million tonnes. The steam cracking route accounts for more than 98 % of ethylene, and 75 % of propylene, production. There are currently some 50 steam crackers in Europe. The average European plant size is around 400 kt/yr and the largest are close to one million tonnes per year. Suitable feedstocks for olefins production range from light gases (e.g. ethane and LPGs) to the refinery liquid products (naphtha, gas-oil). Heavier feedstocks generally give a higher proportion of co-products (propylene, butadiene, benzene) and need larger / more complex plants. All lower olefins are sold on product specification rather than performance and this promotes international markets where selling price is the dominant factor. Steam cracking plants use proprietary technology licensed from a small number of international engineering contractors. The generic designs are similar but specific process details, especially in the furnace area, are dictated by feedstock choice / properties. Global competition has ensured that no one technology gives a major performance advantage and technology selection is typically influenced by previous experience, local circumstances and total installed capital cost.

Applied process: The steam cracking process is highly endothermic (15 to 50 GJ/t ethylene), with the ‘cracking’ reactions taking place in pyrolysis furnaces at temperatures above 800°C. In contrast, the subsequent recovery and purification of olefin products involves cryogenic separation at temperatures down to –150°C and pressures of 35 bar. Plant designs are highly integrated for energy recovery. The highly volatile and flammable nature of the feedstocks / products demands a high standard of overall plant containment integrity, including the extensive use of closed relief systems, resulting in a total hydrocarbon loss over the cracker as low as 5 to 15 kg/t ethylene in the best performing plants.

Consumption / emissions: The large scale of steam cracking operations means that potential emissions are significant.

Air. Pyrolysis furnaces burn low-sulphur gases (often containing hydrogen) and combustion emissions (CO_2, CO, NOx) account for the majority of process air emissions. Emissions of sulphur dioxide and particulates occur from the use, as fuel, of less valuable cracker products (e.g. in auxiliary boilers or other process heaters) and the combustion of coke deposited on furnace coils. VOC emissions may arise from combustion processes, fugitive losses and point source losses from atmospheric vents.

Water. In addition to general effluents (e.g. boiler feed water) there are three specific effluent streams, namely; process water (dilution steam blow-down), spent caustic and decoke drum spray water (where installed). Streams that have been in contact with hydrocarbon fluids may contain pollutants such as: hydrocarbons; dissolved inorganic solids and particulates; materials with a chemical or biological demand for oxygen, and trace quantities of metal cations.

Solid wastes. Relatively little solid waste is generated in the steam cracking process when the feedstock is gas or naphtha, although oily sludges are generated when using gas-oil feed. Most solid wastes are organic sludge and coke, but spent catalysts, adsorbents and various solvents may require periodic disposal.

Best Available Techniques:
Process selection: The steam cracking process is the only large-scale process currently available for producing the full range of lower olefins and it is generally BAT. There is not a BAT feedstock although emissions from plants using gas feedstock tend to be lower than from plants using naphtha or gas oil.

Emissions to Air. The selection, maintenance and operation of efficient pyrolysis furnaces represent the single most important BAT for minimising atmospheric emissions. Modern furnaces have thermal efficiencies in the range 92 – 95 % and utilise natural gas, or more typically residue gas (a mixture of methane and hydrogen). Furnaces incorporate advanced control systems for efficient combustion management and are equipped with either ultra-low NOx burners (giving BAT-associated emissions of 75 - 100 mg NOx/Nm^3 - hourly average) or Selective Catalytic DeNOx units (BAT-associated emissions of 60 - 80 mg NOx/Nm^3 - hourly average). BAT-associated ammonia emissions from modern SCR units are <5 mg/m^3 (hourly average) at high NOx reduction rates but higher emissions may occur as the catalyst ages.

Cracking furnaces require to be periodically decoked using an air/steam mixture. The decoking vent gas can be routed either to the furnace fireboxes or to a separate decoke drum, where emissions of particulates can be controlled to less than 50 mg/Nm^3 (hourly average) by the use of spray water or cyclone recovery systems.

High capacity, elevated flare stacks are a characteristic of ethylene plants since they provide a safe disposal route for hydrocarbons in the event of a major plant upset. Flaring not only creates an environmental impact (visibility, noise) but also represents a significant loss of value to the operator. BAT is therefore to minimise flaring through the use of proven, highly reliable plant and equipment, provision of recycle facilities for material sent to flare and alternative disposal routes (e.g. into other parts of the process stream for out-of-specification material). The development and use of good management practices for the operation and maintenance of the assets also play an important role in maximising performance and hence minimising emissions. Continuous monitoring by closed circuit television, automated flow-ratio controlled steam injection, and pilot flame detection are BAT to minimise the duration and magnitude of any flaring event. Under optimum conditions, the combustion efficiency in flares is 99 %.

Acid gases, including carbon dioxide and sulphur dioxide, are removed from the cracked gas by reaction with sodium hydroxide (in some cases having first reduced the acid gas loading by the use of regenerable amine scrubbing). A sour gas emission may be present if the plant is not able to recover its spent caustic stream, or use wet air oxidation techniques to treat the stream prior to disposal to aqueous effluent. When the spent caustic is treated by acidification, gaseous hydrogen sulphide is created which is either sent to a suitable incinerator (where it is combusted to sulphur dioxide) or more rarely sent to a nearby Claus unit for sulphur recovery.

BAT is to avoid the use of atmospheric vents for the storage and handling of volatile hydrocarbons. BAT for the minimisation of fugitive emissions is the extensive use of welded piping, the utilisation of high integrity seal systems for pumps / compressors, and appropriate gland packing materials for isolation / control valves, backed up by effective management systems for emission monitoring and reduction through planned maintenance.

Emissions to Water. BAT for aqueous effluents is the application of process integrated techniques and recycling / further processing to maximise recovery before final treatment.

- BAT for the process water stream (effluent from the condensation of dilution steam used in the cracking furnaces) is a dilution steam generation facility, where the stream is washed to remove heavy hydrocarbons, stripped and revaporised for recycling to the furnaces.
- BAT for the spent caustic stream may be recovery, wet air oxidation, acidification (followed by sulphur recovery or incineration) or sour gas flaring.
- BAT for final effluent treatment includes physical separation (e.g. API separator, corrugated plate separator) followed by polishing (e.g. hydrogen peroxide oxidation or biotreatment). The BAT levels for final water emissions (as daily averages) are, *inter alia*: COD 30 – 45 mg/l and TOC 10 - 15 mg/l (2 - 10 g/t ethylene).

By-products / wastes. BAT includes: periodic removal of organic wastes such as sludges from API separators for disposal by incineration using specialist disposal contractor; spent catalyst and desiccant for disposal to landfill after reclamation of precious metal; and coke fines for disposal in an immobilised form to landfill and/or incineration.

Illustrative process: Aromatics (Chapter 8)

General information: The term ‘aromatics’ describes benzene, toluene, mixed xylenes, ortho-xylene, para-xylene, meta-xylene (commonly known as BTX). Benzene is used to produce styrene, cumene and cyclohexane. Most toluene is used to produce benzene, phenol and toluene diisocyanate. Para-xylene is transformed into polyethylene terephtalate (PET), mixed xylenes are mainly used as solvents and ortho-xylene is used to make phthalic anhydride.

In 1998 the West European aromatics industry produced over 10 million tonnes with a value of $2.3 billion. The aromatics market is complex and volatile as it concerns six main products that are produced from very different processes and feedstocks. The market prices of aromatics products are linked to each other and also depend on the crude oil cost, naphtha price and exchange rates. In addition, the European Union’s Auto-Oil Directive has, since 01/01/2000, restricted the benzene content of gasoline to <1 % and the subsequent need to recover benzene from upstream feedstocks has caused EU benzene production to increase.

Applied process: BTX aromatics are produced from three main feedstocks: refinery reformates, steam cracker pyrolysis gasoline (pygas) and benzol from coal tar processing. The feedstocks are a mix of aromatics that have to be separated and purified for the chemical market.

- *Benzene:* In Europe, 55 % of benzene comes from pygas, 20 % from reformate, a few percent from coal tar and the balance from chemical treatment of other aromatics. Europe has 57 production units with a combined capacity of 8100 kt/yr.
- *Toluene:* In Europe, pygas and reformate feedstocks each account for 50 % of toluene production. The 28 production units have a combined capacity of 2760 kt/yr.
- *Xylene:* Reformate is the main source of xylenes. Xylenes production normally focuses on para-xylene, but most producers also extract ortho-xylene and meta-xylene. Europe has 11 production units with a combined capacity of 1850 kt/yr.

The choice of production process is a strategic decision that depends on the feedstock availability and cost, and the demand for aromatic products. Such are the variations of feedstock and desired products that each aromatic plant has an almost unique configuration. However, aromatics production from a petrochemical feedstock will utilise some, or all, of a set of closely connected and integrated unit processes that allow:

- The separation of aromatics (from non-aromatics) and the isolation of pure products, using sophisticated physical separation processes (e.g. azeotropic distillation, extractive distillation, liquid-liquid extraction, crystallisation by freezing, adsorption, complexing with BF_3/HF). The most widely used methods are solvent extraction followed by distillation.
- Chemical conversion to more beneficial products using such techniques as: -
  - toluene to benzene by hydrodealkylation (THD or HDA)
  - toluene to benzene and xylene by toluene disproportionation (TDP)
  - xylene and/or m-xylene to p-xylene by isomerisation.

Aromatics production units may be physically located in either refinery or petrochemical complexes and process integration allows the common use of utilities, by-product handling and common facilities such as flare systems and waste water treatment. Most of the aromatic processes are built and designed by international technology providers. There are more than 70 process licences and over 20 licensors, each with different feedstocks and process characteristics to suit local conditions.

Consumption / emissions: Energy consumption will depend on the aromatics content of the feedstock, the extent of heat integration and the technology. Aromatics production processes can be exothermic (e.g. hydrotreating) or energy intensive (e.g. distillation) and there are many opportunities to optimise heat recovery and use.

Emissions from aromatics plants are mainly due to the use of utilities (e.g. heat, power, steam, cooling water) needed by the separation processes. Process designs do not normally incorporate venting to atmosphere and the few emissions from the core process are due to the elimination of impurities, inherent waste streams generated during processing and emissions from equipment.

Best available techniques: It is not possible to identify a BAT process since process selection is so dependent on the available feedstock and the desired products.

Air emissions: BAT is an appropriate selection or combination of, *inter alia*, the following techniques:

- optimise energy integration within the aromatics plant and surrounding units
- for new furnaces, install Ultra Low NOx burners (ULNBs) or, for larger furnaces, catalytic De-NOx (SCR). Installation on existing furnaces depends on plant design, size and layout
- route routine process vents and safety valve discharges to gas recovery systems or to flare
- use closed loop sample systems to minimise operator exposure and to minimise emissions during the purging step prior to taking samples
- use ‘heat-off’ control systems to stop the heat input and shut down plants quickly and safely in order to minimise venting during plant upsets
- use closed piping systems for draining and venting hydrocarbon containing equipment prior to maintenance, particularly when containing >1 wt% benzene or >25 wt% aromatics
- on systems where the process stream contains >1 wt% benzene or >25 wt% total aromatics, the use of canned pumps or single seals with gas purge or double mechanical seals or magnetically driven pumps
- for rising stem manual or control valves, fit bellows and stuffing box, or use high-integrity packing materials (e.g. carbon fibre) when fugitive emission affect occupational exposure
- use compressors with double mechanical seals, or a process-compatible sealing liquid, or a gas seal, or sealless models
- combust hydrogenation off-gases in a furnace with heat recovery facilities

- provide bulk storage of aromatics in[EC DGXI, 1990 #16] double seal floating roof tanks (not for dangerous aromatics such as benzene), or in fixed roof tanks incorporating an internal floating roof with high integrity seals, or in fixed roof with interconnected vapour spaces and vapour recovery or absorption at a single vent
- vents from loading or discharging aromatics to use closed vent systems, bottom-loading and passing evolved vapours to a vapour recovery unit, burner or flare system.

Water emissions: BAT is an appropriate selection or combination of, *inter alia,* the following techniques:

- minimise waste water generation and maximise waste water re-use.
- recover hydrocarbons (e.g. using steam stripping) and recycle the hydrocarbons to fuel or to other recovery systems, and biologically treat the water phase (after oil separation).

Wastes: BAT is an appropriate selection or combination of, *inter alia,* the following techniques:

- recover and re-use the precious metal content of spent catalysts and landfill catalyst support
- incinerate oily sludges and recover the heat
- landfill or incinerate spent clay adsorbents.

Illustrative process: Ethylene Oxide / Ethylene Glycol (Chapter 9)

General information: Ethylene oxide (EO) is a key chemical intermediate in the manufacture of many important products. The main outlet is to ethylene glycols (EG) but other important outlets are ethoxylates, glycol ethers and ethanol amines.

The total European Union production capacity of EO (ex-reactor) is in the order of 2500 kt/yr and is produced at 14 manufacturing sites. Roughly 40 % of this EO is converted into glycols (globally this figure is about 70 %). European installations typically have integrated production of both EO and EG. EO and MEG are sold on chemical specification, rather than on performance in use, and competition is therefore based heavily on price.

Ethylene oxide is toxic and a human carcinogen. EO gas is flammable, even without being mixed with air, and can auto-decompose explosively. Ethylene glycols are stable, non-corrosive liquids that can cause slight eye irritation, or, with repeated contact, skin irritation.

Applied process: Ethylene oxide is produced from ethylene and oxygen (or air) in a gas phase reaction over a silver catalyst. The catalyst is not 100 % selective and part of the ethylene feed is converted to CO_2 and water. The reaction heat released in the EO reactors is recovered by generating steam which is used for heating purposes in the plant. EO is recovered from the gaseous reactor effluent by absorption in water followed by concentration in a stripper. In the oxygen process, part of the recycle gas from the EO absorber is routed through a column in which carbon dioxide is removed by absorption (in a hot potassium carbonate solution) and subsequently removed from the carbonate solution in a stripper.

Ethylene glycols are produced by reacting EO with water at an elevated temperature (typically 150 - 250 °C). The main product is Mono Ethylene Glycol (MEG) but valuable co-products are Di Ethylene Glycol (DEG) and Tri Ethylene Glycol (TEG). MEG is mainly used for the manufacture of polyester fibres and polyethylene terephthalate (PET).

Consumption / emissions: The selectivity of the EO catalyst can have a significant impact on raw material and energy consumption, and on the production of gaseous and liquid effluents, by-products and wastes. The main effluent streams from the EO / EG process are:

- The **CO_2 vent** provides the purge for the CO_2 (and traces of ethylene and methane) formed in the EO reactor. It is recovered for sale or thermally / catalytically oxidised.
- The **inerts vent** provides the purge for inerts present in the ethylene and oxygen feedstocks. The vent mainly contains hydrocarbons and is typically used as fuel gas.

- The **heavy glycols** by-product stream can often be sold to customers.
- The **water bleed** is the combined water effluent of the total EO/EG unit and is sent to a biotreater to degrade the small amounts of water-soluble hydrocarbons (mostly glycols).
- The main source of **solid waste** is spent EO catalyst (which is periodically replaced as activity and selectivity decline). Spent EO catalyst is sent to an external reclaimer for silver recovery and the inert carrier is disposed of.

Best available techniques:
Process route: The BAT process route for **ethylene oxide** is the direct oxidation of ethylene by pure oxygen (due to the lower ethylene consumption and lower off-gas production). The BAT process route for **ethylene glycol** is based on the hydrolysis of EO (with reaction conditions to maximise production of the desired glycol(s) and minimise energy consumption).

Emissions to Air: The techniques to prevent the loss of EO containment, and hence occupational exposure to EO, are also BAT to provide environmental protection.

BAT for the CO_2 vent is recovery of the CO_2 for sale as a product. Where this is not possible, BAT is to minimise CO_2, methane and ethylene emissions by applying more efficient oxidation catalyst, reducing methane and ethylene levels before CO_2 stripping, and/or routing the CO_2 vent to a thermal / catalytic oxidation unit.

BAT for the inerts vent is transfer to a fuel gas system for energy recovery, or flaring (typically reducing EO emission levels to < 1 mg EO/Nm^3 - hourly average). If the EO reaction is carried out using air rather than pure oxygen, then BAT is to transfer the inerts excess to a second oxidation reactor to convert most of the residual ethylene into EO.

BAT for EO containing vent gases is:
- water scrubbing to <5 mg EO/Nm^3 (hourly average) and release to atmosphere (for vents with a low content of methane and ethylene)
- water scrubbing and recycle to the process (for vent streams with a noticeable content in methane and ethylene)
- minimisation techniques (e.g. pressure balancing & vapour return in storage / loading)

Emissions to Water: BAT for reducing emissions to water is to concentrate partial contributor streams with recovery of a heavy organic stream (for sale or incineration) and route the remaining effluent stream to a biological treatment unit. The application of BAT allows an emission level of 10 - 15g TOC/t EO ex-reactor to be achieved.

By-products and Wastes:
- BAT for heavy glycols is to minimise formation in the process and to maximise possible sales, in order to minimise disposal (e.g. by incineration).
- BAT for spent EO catalyst is optimising catalyst life and then recovery of the silver content prior to appropriate disposal (e.g. landfill).

Illustrative process: Formaldehyde (Chapter 10)

General information: Formaldehyde is widely used for the manufacture of numerous products (e.g. resins, paints), either as 100 % polymers of formaldehyde or a reaction product together with other chemicals. The total European production capacity of 3100 kt/yr is provided by 68 units in 13 Member States. Formaldehyde is toxic and a suspected carcinogenic at high concentrations, but the strong irritating effect means that human exposure to high concentrations is self-limiting. Strict operational practices have also been developed to limit the occupational exposure of workers.

Applied process: Formaldehyde is produced from methanol, either by catalytic oxidation under air deficiency (‘silver process’) or air excess (‘oxide process’). There are further options to design the silver process for either total or partial methanol conversion. The process routes all have advantages and disadvantages and European formaldehyde production capacity is split roughly equally between the silver and oxide routes.

Consumption / emissions: Electricity and steam are the two main utilities and their consumption is directly linked to process selectivity. The process selectivity is, in turn, a function of the carbon loss (as CO and CO_2) in the reactors. The lower the carbon loss, the higher the selectivity. However, the full oxidation of carbon is very exothermic (compared to the reactions producing formaldehyde) so high carbon loss produces more steam. A poor catalyst therefore produces large quantities of steam but is detrimental to methanol consumption.

Air emissions: For both the silver and oxide processes, the off-gas from the formaldehyde absorption column is the only continuous waste gas stream. The main pollutants are formaldehyde, methanol, CO and dimethyl ether. Further emissions may arise from storage breathing and fugitives.

Water emissions: Under routine operating conditions, the silver and oxide processes do not produce any significant continuous liquid waste streams. Many of occasional arisings can be reworked into the process to dilute the formaldehyde product.

Wastes: There is little formation of solid wastes under normal operating conditions, but there will be spent catalyst, build-up of solid para-formaldehyde and spent filters.

Best available techniques: The BAT production route can be either the oxide or the silver process. Process selection will depend on factors such as: methanol consumption and price; plant production capacity; physical plant size; electricity use; steam production; and catalyst price / life. BAT is to optimise the energy balance taking into account the surrounding site.

Air emissions:

- BAT for vents from the absorber, storage and loading / unloading systems is recovery (e.g. condensation, water scrubber) and / or treatment in a dedicated or central combustion unit to achieve a formaldehyde emission of < 5 mg/Nm^3 (daily average)
- BAT for absorber off-gases in the **silver process** is energy recovery in a motor engine or thermal oxidiser to achieve emissions of:
    - carbon monoxide 50 mg/Nm^3 as a daily average (0.1 kg/t formaldehyde 100 %)
    - nitrogen oxides (as NO_2) 150 mg/Nm^3 as a daily average (0.3 kg/t formaldehyde 100 %)
- BAT for reaction off-gas from the **oxide process** is catalytic oxidation to achieve emissions of: carbon monoxide <20 mg/Nm^3 as a daily average (0.05 kg/t formaldehyde 100 %) and nitrogen oxides (as NO_2) <10 mg/Nm^3 as a daily average
- BAT for the design of methanol storage tanks is to reduce the vent streams by such techniques as back-venting during loading/unloading.
- BAT for the vents from the storage of methanol and formaldehyde include: thermal / catalytic oxidation, adsorption on activated carbon, absorption in water, recycling to the process, and connection to the suction of the process air blower.

BAT for **waste water** is to maximise re-use as dilution water for the product formaldehyde solution or, when re-use is not possible, biological treatment.

BAT for **catalyst waste** is to first maximise the catalyst life by optimising reaction conditions and then to reclaim the metal content of any spent catalyst.

BAT for the build-up of solid **para-formaldehyde** is to prevent formation in process equipment by optimising heating, insulation and flow circulation, and to reuse any unavoidable arisings.

Illustrative process: Acrylonitrile (Chapter 11)

General information: Acrylonitrile is an intermediate monomer used world-wide for several applications. The majority of European acrylonitrile is used in the production of acrylic fibre, with ABS representing the next most important end user. The EU has seven operational production installations and these account for a nameplate capacity of 1165 kt/yr.

Applied process: The BP/SOHIO process accounts for 95 % of world-wide acrylonitrile capacity and is used in all EU plants. The process is a vapour phase, exothermic ammoxidation of propylene using excess ammonia in the presence of an air-fluidised catalyst bed. Several secondary reactions take place and there are three main co-products, namely:

- hydrogen cyanide, which is either transformed into other products on site; sold as a product (if a use is available); disposed of by incineration; or a combination of all three
- acetonitrile, which is purified and sold as a product, and/or disposed of by incineration
- ammonium sulphate, which is either recovered as a product (e.g. as a fertiliser), or destroyed elsewhere on site.

The consumption of raw materials and energy in the acrylonitrile process are influenced by such factors as catalyst selection, production rate and recovery plant configuration. Propylene and ammonia are the major raw materials but ‘make-up’ catalyst is also a significant consumable.

Propylene ammoxidation is a highly exothermic reaction. Acrylonitrile plants are generally net exporters of energy as the heat of reaction is used to generate high-pressure steam that is often used to drive air compressors and provide energy to downstream separation / purification units. The energy export range is 340 - 5700 MJ/t acrylonitrile and so site-wide energy management is a key issue.

Water is produced in the reaction step and rejection of water from the process is a critical part of plant design. There are many differing techniques and, in a widely used one, the key step involves concentrating the contaminant in the water stream using evaporation. The concentrated, contaminated stream may be burnt or recycled to other parts of the process to maximise recovery of saleable products (before burning the contaminated stream). The ‘clean’ water stream recovered from the concentration processes is further treated, normally in biological waste water treatment plants.

The reaction off-gases from the process absorber contains non-condensables (e.g. nitrogen, oxygen, carbon monoxide, carbon dioxide, propylene, propane) as well as vaporised water and traces of organic contaminants. Thermal or catalytic oxidation can be used to treat this stream.

An acrylonitrile plant may have facilities to incinerate process residues and also to burn hydrogen cyanide. The magnitude and composition of flue gases will depend on the use of external facilities and the availability of hydrogen cyanide consumers. There is usually no specific treatment of the flue gas (except for heat recovery).

Owing to the hazardous properties of acrylonitrile and hydrogen cyanide, safety considerations are very important in their storage and handling.

Best Available Techniques: The BAT process is based on the ammoxidation of propylene in a fluid bed reactor, with subsequent recovery of acrylonitrile. Recovery for sale of the main co-products (hydrogen cyanide, acetonitrile and ammonium sulphate) may be BAT depending on local circumstances, but backup recovery / destruction facilities are needed in all cases.

BAT for the absorber off-gas is to reduce the volume through the development of more efficient catalyst and optimised reaction / operation conditions. BAT is then destruction of the organics (to a target acrylonitrile concentration of < 0.5 mg/Nm^3 - hourly average) in a dedicated thermal or catalytic oxidiser, or in a common purpose incinerator or in a boiler plant. In all cases BAT will include heat recovery (normally with steam production).

BAT for the miscellaneous vent streams is treatment in either the absorber off-gas treatment system or a common flare system for total destruction of the organics. Other vent streams may be scrubbed (to a target acrylonitrile concentration of < 5 mg/Nm^3 - hourly average) to allow recycling of recovered components.

Contaminated aqueous effluent streams include effluent from the quench section (containing ammonium sulphate), stripper bottoms stream and discontinuous streams. BAT includes the crystallisation of ammonium sulphate for sale as fertilisers.

BAT for the water streams is pre-treatment by distillation to reduce the light hydrocarbons content and to concentrate or separate heavy hydrocarbons, with the aim of reducing the organics load prior to final treatment. BAT for the recovered light and heavy hydrocarbon streams is further treatment to recover useful components (e.g. acetonitrile) prior to combustion with energy recovery.

BAT for aqueous waste streams is to treat the contaminated effluent stream in a dedicated, central or external waste water treatment plant including biotreatment, to take advantage of the high biodegradability of the organic contaminants. The emission level associated with BAT is 0.4 kg Total Organic Carbon /t acrylonitrile.

Illustrative process: EDC / VCM (Chapter 12)

General information: EDC (1,2 ethylene dichloride) is mainly used for the production of VCM (Vinyl Chloride Monomer) and VCM is itself used almost exclusively in the manufacture of PVC (Polyvinyl Chloride). The EDC/VCM process is often integrated with chlorine production sites because of the issues with chlorine transportation and because the EDC/VCM/PVC chain is the largest single chlorine consumer. The European Union has 30 EDC/VCM production sites with a total VCM capacity of 5610 kt/yr.

Applied process: In the ethylene-based process, EDC is synthesised by the chlorination of ethylene (by high or low temperature direct chlorination) or by the chlorination of ethylene with HCl and oxygen (oxychlorination). Crude EDC product is washed, dried and purified with the off-gases passing to catalytic or thermal oxidation. Pure, dry EDC is thermally cracked in cracking furnaces to produce VCM and HCl, and the VCM is purified by distillation (HCl and unconverted EDC removal).

When all the HCl generated in EDC cracking is re-used in an oxychlorination section, and when no EDC or HCI is imported or exported, then the VCM unit is called a ‘balanced unit’. By using both direct chlorination and oxychlorination for EDC production, balanced units achieve a high level of by-product utilisation. There are opportunities for energy recovery and re-use because of the combination of highly exothermic reactions (direct chlorination and oxychlorination) and energy users (EDC cracking, EDC and VCM separations).

Consumption / emissions: The main raw materials are ethylene, chlorine, oxygen (air) and, dependent on process configuration, energy.

VCM, as a carcinogen, is the **air** pollutant of most concern, but other potential pollutants include EDC, chlorinated hydrocarbons (e.g. carbon tetrachloride).

The main **water** pollutants are volatile and non-volatile chlorinated organic compounds (e.g. EDC), organic compounds and copper catalyst.

The EDC distillation train generates **liquid residues** containing a mixture of heavies (e.g. chlorinated cyclic or aromatic compounds including dioxin-related components (predominantly the octo-chlorodibenzofuran congener from oxychlorination) with suspended iron salts from catalysts) and lights (C_1 and C_2 chlorinated hydrocarbons).

The main **solid wastes** are spent oxychlorination catalyst, direct chlorination residues, coke from thermal cracking and spent lime (used in some plants for VCM neutralisation).

Best available techniques: In terms of **process selection** the following are BAT:

- for the overall production of EDC/VCM, BAT is the chlorination of ethylene.
- for the chlorination of ethylene, BAT can be either direct chlorination or oxychlorination.
- for direct chlorination, BAT can be either the low or high-temperature variants.
- for ethylene oxychlorination there are choices of oxidant (oxygen is BAT for new plants and can be for existing air-based plants) and reactor type (fixed and fluid bed are both BAT).
- optimise process balancing (sources and sinks of EDC/HCl) to maximise the recycle of process streams and aim for full process balancing.

Air pollutants: BAT for the main process vents is to:

- recover ethylene, EDC, VCM and other chlorinated organic compounds by direct recycling; refrigeration / condensation; absorption in solvents; or adsorption on solids.
- use thermal or catalytic oxidation to achieve off-gas concentrations (as daily averages) of: EDC + VCM <1 mg/Nm^3, dioxin < 0.1 ng iTEQ/Nm^3, HCl <10 mg/Nm^3
- recover energy and HCl from the combustion of chlorinated organic compounds
- use continuous on-line monitoring of stack emissions for O_2 and CO and periodic sampling for C_2H_4, VCM, EDC, Cl_2, HCl and Dioxin.

BAT for fugitives is to use techniques that achieve releases of volatile chlorinated hydrocarbons < 5 kg/h, EDC in working atmosphere <2 ppm, and VCM in working atmosphere <1 ppm.

Water pollutants: BAT for effluent pre-treatment is:

- steam, or hot air, stripping of chlorinated organic compounds to concentrations of <1 mg/l, with off-gas passing to condensation and recovery, or incineration
- flocculation, settling and filtration of semi- or non-volatile chlorinated organic compounds that are adsorbed on particulates
- alkaline precipitation and settling (or electrolysis) to a copper concentration < 1 mg/l.

BAT for effluent final treatment is biological treatment to achieve: total chlorinated hydrocarbons 1 mg/l, total copper 1 mg/l, COD 125 mg/l (50 - 100 with dual nitrification-de-nitrification), dioxins 0.1 ng iTEQ/l, hexachlorobenzene + pentachlorobenzene 1 µg/l, hexachlorobutadiene 1 µg/l.

BAT for by-products (residues) is to minimise formation through the choice of catalysts and operating conditions and to maximise the re-use of by-products as feedstock.

BAT for wastes is minimisation and recycling to the process. BAT for sludge from waste water treatment and coke from EDC cracking is incineration in a dedicated or multi-purpose hazardous waste incinerator.

Illustrative Process: Toluene Diisocyanate (Chapter 13)

General information: Isocyanates, especially toluene diisocyanate (TDI), are commercially important in the production of polyurethanes (e.g. for flexible foams, plastics and paints for furniture, cars and consumer products). In 1991 the world-wide TDI production capacity was estimated at 940 kt. The 2001 European production capacity is 540 kt/year with plants in Belgium, Germany, France and Italy.

Applied process: Process steps in the manufacture of TDI are the nitration of toluene, the hydrogenation of dinitrotoluene (DNT) and phosgenation of the resulting toluene amine (TDA) in a solvent. The choice of reaction conditions during the phosgenation is important because of the reactivity of isocyanate groups and the possibility of side reactions.

Consumption / emissions: The inputs are primarily toluene and nitrating acid (to produce the intermediate DNT), hydrogen (for the hydrogenation of DNT to TDA) and phosgene (for the phosgenation of the TDA to TDI). Process solvents and catalysts are mainly re-used. The main air pollutants are organic compounds (e.g. toluene, TDA, solvents), NOx and HCl. The main water pollutants are organic compounds (e.g. nitroaromatics) and sulphates. The hydrogenation process produces distillation residues and spent catalysts. The phosgenation unit produces distillation residues, contaminated solvents and activated carbon that are disposed of by incineration.

Best Available Techniques: The BAT process design is based on the phosgenation of toluene.

BAT for consumption and re-use:
- optimise the re-use of hydrogen chloride and of sulphuric acid (DNT manufacture)
- optimise the energy re-use of the exothermic reaction (without compromising yield optimisation) and of the waste gas incineration (e.g. recuperative incinerator).

BAT for waste gases is the treatment with scrubbers (in particular for phosgene, hydrogen chloride and VOC removal) or thermal incineration of organic compounds and nitrogen oxides. Low concentrations of organics can be treated by other techniques such as activated carbon. Nitrogen oxides can be also minimised by partial oxidation. BAT is also every equivalent combination of treatment methods. Emission concentrations (as hourly averages) associated with these techniques are: <0.5 mg/m^3 phosgene, <10 mg/m^3 hydrogen chloride and, for incineration, <20 mg total carbon /m^3.

BAT for the waste water from nitration is:
- reduction of waste water and nitrate / nitrite emission by optimising the DNT process (waste water volume < 1 m^3/t)
- maximise the re-use of process water
- removal of nitroaromatic compounds (DNT, Di/Tri-Nitrocresols) to reduce organic load (< 1 kg TOC /t DNT) and to ensure biodegradability (>80 % elimination by Zahn-Wellens test). Final biological treatment to remove COD/TOC and nitrate
- incineration (*in lieu* of waste water pre-treatment and biological treatment).

BAT for the waste water from hydrogenation is:
- removal of nitroaromatic compounds by stripping, distillation and /or extraction of effluents
- re-use of pre-treated process water. Waste water volume < 1 m^3/t TDA
- Incineration (*in lieu* of waste water pre-treatment and biological treatment).

BAT for the waste water from phosgenation is:
- optimise the process to give a TOC load of <0.5 kg/t TDI prior to biological treatment.

BAT for plant safety is partial containment of the most hazardous elements of the phosgenation process or mitigation measures (e.g. steam/ammonia curtain) for accidental phosgene release.

The **Concluding remarks (Chapter 14)** of the BREF consider that the LVOC information exchange was generally very successful. A high degree of consensus was reached and there are no split views in this document. Much information was made available and there was a high degree of participation by industry and Member States. Due to the diversity of LVOC processes, the BREF does not give a very detailed examination of the whole LVOC sector but makes a good first attempt at defining BAT generically and for the chosen illustrative processes.

Key dates in the information exchange were the 1997 'Paris Workshop', the TWG kick-off meeting in April 1999 and the second TWG meeting in May 2001. Drafting of the BREF took longer than envisaged because of delays experienced by TWG members in compiling data and writing contributory reports. A first draft was issued in July 2000 and received almost 800 TWG comments - all of them electronically. This enabled much easier handling of the comments and, when subsequently annotated with EIPPCB decisions, it also provided a transparent record of how and why comments had been implemented. A second draft of the BREF was issued in December 2000 and received 700 comments.

The most significant discussion points have been the agreement of Generic BAT for air and water pollutants that is flexible enough to cover all LVOC processes and yet specific enough for permit writing purposes. This was hampered by a lack of emission / cost data and the simultaneous drafting of horizontal BREFs (most notably the BREF on 'Waste water / waste gas management / treatment in the chemical industry').

Over 150 items of technical material were submitted to the information exchange and there was a generally good spread of information over the LVOC industrial sectors. The illustrative process chapters of the BREF owe much to the reports submitted by CEFIC and their considerable efforts in co-ordinating European process reviews (often for the very first time). Other significant contributions were received from, in no order of importance, Austria, Finland, Germany, Italy, the Netherlands, Sweden and the UK.

Over 140 working documents were placed on the Members' Workspace of the EIPPCB web-site and, as of the second TWG meeting (May 2001), these documents had, in total, been accessed on over 1000 occasions. This demonstrates a highly active TWG that made good use of the electronic exchange forum provided by the Members' Workspace.

The LVOC sector uses well-established processes and the chapter on **Emerging Techniques (Chapter 15)** does not identify any imminent technological changes. There seems to be no pressing need for BREF revision but this should be reviewed in light of BREF usage (especially the Generic BAT chapter). A number of topics are recommended for consideration in future information exchanges, namely:

- Illustrative processes – priority consideration should be given to processes for the production of 2-ethyl hexanol, phenol, adipic acid and major LVOC products such as ethylbenzene, styrene and propylene oxide. It is also recommended to review coverage of the TDI process and to consider a selection methodology for illustrative processes.
- Interface with other BREFs – review the LVOC BREF for gaps / overlaps once there is a complete series of horizontal and chemical industry BREFs.
- Whole Effluent Assessment – may have greater value for LVOC waste waters.
- Emission / consumption data - collect more quantitative data and establish environmental benchmark methodologies.
- Cost data – collect more cost data and help develop a standard cost conversion method.
- Other pollutants / issues – provide more information on the topics of vibration, noise, decommissioning and accident prevention.
- Chemical strategy – consider how the BREF interfaces with the EU chemicals risk reduction strategy.
- Separate illustrative process documents – consider if the BREF is better divided into a core 'generic' document and a number of detailed 'illustrative process' documents.
- Classification system for air pollutants – the Environment DG are recommended to consider the need for a standard European classification system for air pollutants.
- Wider value of illustrative processes – consider if the 'thumbnail' process descriptions and Generic BAT need expanding to provide more information on non-illustrative processes.
- Biotechnology – is recommended as a field that warrants further research and development.
- Thresholds leak rates for the repair of fugitive losses – consideration of the different views of CEFIC and the Netherlands with a view to establishing a common approach.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the EIPPCB of any research results which are relevant to the scope of this document (see also the preface of this document).