

Technical  
Guidance

IPC S2 4.01

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Process Guidance

# Large Volume Organic Chemicals

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# Processes Subject to Integrated Pollution Control

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Series 2 (S2)  
Chemical Industry Sector

S2 4.01: Large - Volume Organic Chemicals

Prepared by the Environment Agency 1999



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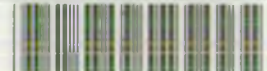
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## Executive Summary

This IPC Guidance Note is issued by the Environment Agency as one of a series of guidance notes for processes prescribed for Integrated Pollution Control (IPC) in Regulations made under Section 2 of the Environmental Protection Act 1990 (EPA90). It is a guide on techniques and standards relevant to petrochemical and other large-volume organic chemical manufacture. It supersedes Her Majesty's Inspectorate of Pollution's Chief Inspector's Guidance Notes IPR 4/1 to IPR 4/4 and IPR 4/6 published by HMSO in 1993.

It will be used by Agency staff, in conjunction with other relevant guidance, in assessing operators' proposals relating to their Authorisations under EPA90. This Note should be used together with separate guidance on monitoring, dispersion methodology and assessment principles for determining Best Available Techniques Not Entailing Excessive Cost (BATNEEC) and Best Practicable Environmental Option (BPEO) to provide a framework for a consistent approach to the regulation of this class of processes regulated under IPC.

The processes covered by this Note are found in Sections 4.1 and 4.2 of the Regulations. Other organic chemical processes prescribed for IPC are covered by IPC Guidance Note S2 4.02.

This Note provides brief descriptions of selected processes, best available techniques for pollution prevention and control, and the levels of release achievable by their use. Economic information on the relevant sectors of the chemical industry is included.

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# 1 Introduction

## 1.1 Scope and status of Guidance Note

This IPC Guidance Note supersedes Her Majesty's Inspectorate of Pollution's Chief Inspector's Guidance Notes IPR 4/1 to IPR 4/4 and IPR 4/6 published by HMSO in 1993. It is issued by the Environment Agency as one of a series of guidance notes for processes prescribed for Integrated Pollution Control (IPC) in Regulations<sup>(1)</sup> made under Section 2 of the Environmental Protection Act 1990 (EPA90). It is a guide on techniques and standards relevant to the processes covered by the Note.

It will be used by Agency staff, in conjunction with other relevant guidance<sup>(2)</sup>, in assessing operators' proposals relating to their Authorisations under EPA90. This Note should be used together with separate guidance on monitoring<sup>(3)</sup>, dispersion methodology<sup>(4)</sup>, and assessment principles for determining Best Available Techniques Not Entailing Excessive Cost (BATNEEC) and the Best Practicable Environmental Option (BPEO)<sup>(5,6)</sup> to provide a framework for a consistent approach to the regulation of this class of IPC process.

This Note represents the state of understanding at the time of writing, and includes:

- description(s) of the principal processes covered by the Note;
- ① the prescribed substances and other substances that can cause harm and are most likely to be released from the processes;
- ⊕ guidance on best available techniques (BATs) for the control of releases;
- ⊖ benchmark release levels;
- ⊙ other environmental standards relevant to the process; and
- information on the economic implications of the relevant pollution control techniques.

An operator should keep up to date with the best available techniques relevant to the process. This Note may not therefore be cited in an attempt to delay the introduction of improved, available techniques, and, except where specifically stated to the contrary, nothing contained herein should be considered prescriptive.

The concepts of BATNEEC and BPEO expressed in the EPA90 and associated Regulations are site-specific. This Note cannot take into account such site-specific considerations. Thus, while operators' proposals should be judged against the benchmark release levels given in this Note, the benchmarks should not be applied as uniform release limits. They are indicative, but not prescriptive, for new processes that the prevention, minimisation and abatement of releases.

Where other release levels are proposed for a specific case, comparing them and the benchmark release levels will indicate the degree of technical and economic justification required to be provided by the operator. Conditions in Authorisations that ensure that all factors, including those which are site-specific, have been taken into account, and that the legal requirements to use BATNEEC and BPEO are fully satisfied.

Notwithstanding the requirements to use BATNEEC and BPEO, compliance with statutory environmental quality standards or objectives, and with agreed international obligations relating to permitted releases or environmental standards, is mandatory. No discretion is permitted without formal policy approval.

## 1.2 Existing processes

Existing processes should have been upgraded taking into account the criteria included in Articles 4, 12 and 13 of the European Community Directive on the Combating of Air Pollution from Industrial Plants known as the Air Framework Directive (84/360/EEC)<sup>(7)</sup>. Article 13 requires the following points to be taken into account:

- ⊕ the plant's technical characteristics;
- its rate of utilisation and remaining life;
- ⊙ the nature and volume of polluting emissions from it; and
- ⊕ the desirability of not entailing excessive costs for the plant concerned, having regard in particular to the economic situation of undertakings belonging to the category in question.

Most existing processes should have completed their improvement programmes and should be achieving the benchmark release levels given in Section 4 or should be closely approaching them. Where this is not so, a timetable for further improving or decommissioning the process should be required.

### 1.3 Processes covered by this Note

This Note covers processes for the manufacture of petrochemicals and organic chemicals produced in large volume. Most, but not all, are continuous processes and relate most closely to those listed in Sections 4.1 and 4.2 of the Regulations<sup>(1)</sup>.

Not all relevant processes operating in the UK can be covered and the Note is not intended to coincide precisely with these sections of the Regulations. Other organic chemical processes prescribed for IPC are covered by IPC Guidance Note S2 4.02.<sup>(2)</sup>

Where other prescribed processes are carried on in conjunction with the primary process, reference should be made to the relevant Chief Inspector's Guidance Notes (CIGNs) or IPC Guidance Notes (IPCGNs) and, where appropriate, the Secretary of State's Guidance for Local Authority Air Pollution Control on the ancillary processes insofar as they have potential for releases to the environment.

In the context of this Note 'process' is from receipt of raw materials via production of intermediates to dispatch of finished products.

### 1.4 Reference conditions used throughout this Note

The reference conditions of substances in releases to air from point sources are: temperature 273 K (0°C), pressure 101.3 kPa (1 atmosphere), no correction for water vapour or oxygen.

These reference conditions relate to the benchmark release levels given in this Note and care should always be taken to convert benchmark and proposed releases to the same reference conditions for comparison. The Authorisation may employ different reference conditions if they are more suitable for the process in question.

To convert measured values to reference conditions see Technical Guidance Note M2<sup>(3)</sup> for more information.

Releases may be expressed in terms of mg/m<sup>3</sup>, g/h, g/t (product) or g/MJ as appropriate.

## 1.5 Standards and obligations

### 1.5.1 The Large Combustion Plant Directive (LCPD)<sup>(4)</sup>

The LCPD is under review. Any changes to the Directive would normally be implemented to agreed European Union and UK Government timetables.

The LCPD applies to any technical apparatus in which fuels are oxidised in order to use the heat thus generated and has a thermal input of 50 MW or more.

The LCPD applies only to combustion plants designed for the production of energy. It does not apply to plants that

make direct use of the products of combustion in manufacturing processes.

In particular, the LCPD does not apply to the following plants:

- plants in which the products of combustion are used for the direct heating, drying, or any other treatment of objects or materials, eg reheating furnaces, furnaces for heat treatment;
- post-combustion plants, ie any technical apparatus designed to purify the waste gases by combustion which is not operated as an independent combustion plant;
- facilities for the regeneration of catalytic cracking catalysts;
- facilities for the conversion of hydrogen sulphide into sulphur;
- reactors used in the chemical industry;
- coke battery furnaces; and
- cowpers.

Plants powered by diesel, petrol and gas engines or by gas turbines, irrespective of the fuel used, are not covered by the LCPD.

The LCPD gives limits for emissions of SO<sub>2</sub>, NO<sub>x</sub> and particulates from new large combustion plant.

### 1.5.2 Air quality standards

Statutory Instrument 1989 No 317, Clean Air, The Air Quality Standards Regulations 1989<sup>(5)</sup> gives limit values in air for the following substances:

- sulphur dioxide;
- suspended particulates;
- lead; and
- nitrogen dioxide.

Any emission from the process should not result in a breach of the appropriate air quality standard beyond the site boundary.

### 1.5.3 Air quality objectives

Statutory Instrument 1997 No 3043, Environmental Protection, The Air Quality Regulations 1997<sup>(6)</sup> gives air quality objectives to be achieved by 2005 for:

- benzene;
- 1,3 - butadiene;

- carbon monoxide;
- lead;
- nitrogen dioxide;
- PM<sub>10</sub>; and
- sulphur dioxide.

#### 1.5.4 The National Plan for reducing emissions of sulphur dioxide (SO<sub>2</sub>) and oxides of nitrogen NO<sub>x</sub><sup>(12)</sup>

This Plan places a limit on the annual emissions of these two substances from existing (in 1987) large combustion plant. These limits decrease over a period of time. The National Plan gives effect to the provisions of the LCPD on existing plant.

#### 1.5.5 The UNECE convention on long-range transboundary air pollution<sup>(13)</sup>

Under this Convention, a requirement further to reduce SO<sub>2</sub> emissions from all sources has been agreed. The second Sulphur Protocol (Oslo, 1994) obliges the UK to reduce SO<sub>2</sub> emissions by 80% (based on 1980 levels) by 2010. Negotiations are now under way which could lead to a requirement further to reduce emissions of NO<sub>x</sub> and volatile organic compounds (VOCs).

#### 1.5.6 Volatile organic compounds

Reducing Emissions of VOCs and Levels of Ground Level Ozone: A UK Strategy<sup>(14)</sup> was published by the Department of the Environment in October 1993. It sets out how the Government expects to meet its obligations under the UNECE VOCs Protocol to reduce its emissions by 30% (based on 1988 levels) by 1999, including the reductions projected for the major industrial sectors. A 65% reduction is forecast for the chemicals sector, based on the application of BATNEEC.

The Montreal Protocol<sup>(15)</sup> concerns substances that deplete the ozone layer. These include chlorinated fluorocarbons, halons, carbon tetrachloride, 1,1,1-trichloroethane and methyl bromide.

EC Directive 90/415/EEC<sup>(16)</sup> covers releases to water from the production and use of 1,2-dichloroethane, trichloroethylene, perchloroethylene and trichlorobenzene. Oslo and Paris Commission (OSPARCOM) Recommendation 96/2<sup>(17)</sup> relates to best available techniques for the manufacture of vinyl chloride monomer (VCM) and 96/3<sup>(18)</sup> suspension poly (vinyl chloride) (PVC).

#### 1.5.7 Water quality standards

Statutory Instrument (1989) No 2286 and (1998) No 389<sup>(19)</sup>, The Surface Waters (Dangerous Substances Classification) Regulations gives the annual mean concentrations limit values for certain substances in receiving waters.

#### 1.5.8 Groundwater protection

The principles, powers and responsibilities for groundwater protection in England and Wales, together with the Agency's policies in this regard, are outlined in the Agency's document "Policy and Practice for the Protection of Groundwater" (PPPG)<sup>(20)</sup>. This outlines the concepts of vulnerability and risk and the likely acceptability from the Agency's viewpoint of certain activities within groundwater protection zones.

The EC Directive on the Protection of Groundwater against Pollution Caused by Certain Dangerous Substances (80/68/EEC)<sup>(21)</sup> imposes an obligation on Member States to prevent the introduction into groundwater of List I substances and to limit the introduction of List II substances so as to prevent pollution of groundwater. The Directive is at present implemented by, inter alia:

- Part I of the Environmental Protection Act 1990, which requires authorisation of IPC processes;
- Part II of that Act, which requires the management of controlled wastes;
- Regulation 15 of the Waste Management Licensing Regulations 1994, which requires the Agency to observe the provisions of the Groundwater Directive when issuing waste management licences; and
- Part II of the Water Resources Act 1991, which makes it an offence to discharge polluting matter to controlled waters, except in accordance with a Consent issued by the Agency.

In addition, the Government is introducing new Groundwater Regulations to provide additional protection and complete the transposition of the Groundwater Directive. In addition to those processes controlled for IPC, these Regulations are intended to relate primarily to activities where List I and II substances are either deliberately discharged, or where there is a risk of discharge occurring, for example, as a result of spillages or leaks. The Regulations will provide for prior investigation of the potential effects of discharges on groundwater; the Authorisation of disposal or tipping to land and Consents to discharge to groundwater; the serving of Notices by the Agency to prohibit activities or to apply conditions; the recognition the importance of Codes of Practice; and provisions for cost recovery by the Agency.

Two key aspects of the Groundwater Directive are the need for the following:

- Prior investigation of the potential effect on groundwater of on-site disposal activities or discharges to groundwater. Such investigations will vary from case to case, but the Agency is likely to require a map of the proposed disposal area; a description of the underlying geology, hydrogeology and soil type, including the depth of saturated zone and quality of groundwater; the proximity of the site to any surface waters and

abstraction points, and the relationship between ground- and surface waters; the composition and volume of waste to be disposed of; and the rate of planned disposal.

- Requisite surveillance. This will also vary from case to case, but may include monitoring of groundwater quality and ensuring that the necessary precautions to prevent groundwater pollution are being undertaken.

The Directive states that, subject to certain conditions, the discharges of List I substances to groundwater may be authorised if the groundwater is permanently unsuitable for other uses'. Advice must be sought from the Agency where this is being considered as a justification for such discharges

The Agency is obliged to take account of these requirements for IPC processes and, where there is an activity that represents a potential risk to groundwater, may request further investigations.

## 2 Processes, potential release routes and specialised techniques for controlling releases

### 2.1 Introduction

Many different processes are covered by this Note and some may provide feedstock for others on a large site. Petrochemical processes are often located next to a refinery and may take feedstock and return some products to it. Utilities such as steam and electricity and services such as effluent treatment may be supplied by the refinery.

Despite the wide range of processes, the key issues are often common. For example, the release of VOCs and the techniques for controlling them are central to all the processes.

It is not possible to include all processes covered by this Note. Selected processes are briefly described and the release routes of pollutants from them are indicated. The control techniques that are considered to be BAT for the process either are listed in Section 3 on general techniques or, where they are special to the process, are described here. Release levels achievable by the use of the techniques are provided in Section 4 for each group of related processes as benchmarks. They should not be applied as uniform release limits.

### 2.2 Petrochemicals

#### 2.2.1 Butadiene

In Western Europe butadiene is manufactured primarily from the C4 stream produced in the cracking operations for ethylene manufacture. The feedstock is a mixture of hydrocarbons, including butadiene, of similar boiling points. Conventional distillation techniques provide insufficient purification and a solvent extraction or extractive distillation process is used in all three main manufacturing variants. Solvents used include aqueous cuprous ammonium acetate (the CAA process), acetonitrile (the ACN process) and *N*-methylpyrrolidone (the NMP process). Each process with its waste streams is described in turn.

##### (a) The CAA process

Mixed C4 hydrocarbons are extracted counter-currently with a 20% CAA solution in a series of mixer-settlers. Distillation of the rich CAA solution at successively increasing temperature liberates the lower-boiling hydrocarbons first and, at 80°C, butadiene, which is purified by redistillation. Polymer build-up in the circulating solvent (which would otherwise cause process problems due to fouling) is reduced by passing it through carbon adsorbers. The C4 feed is pre-treated to remove acetylene, which would otherwise combine with the copper to form explosive complexes.

##### Releases to Air

- Hydrocarbons and ammonia from distillation and storage tank vents.

##### Releases to water

- Copper compounds, ammonia and hydrocarbons as process and solvent wastes to water.

##### Releases to land

- Copper-containing sludges, charcoal and polymerised hydrocarbons.

##### (b) The ACN process

The ACN process comprises feed preparation, extraction, purification, and solvent purification and recovery. Oxygen can initiate unwanted polymerisation and is removed from the feedstock by washing with sodium nitrite solution. Washed hydrocarbons are then distilled to remove C3 hydrocarbons. The vapour-phase mixed hydrocarbons are contacted and absorbed in acetonitrile; butanes and butene remain largely unabsorbed. ACN, rich in butadiene, is distilled and butadiene removed with some butenes, acetylenes and 1,2-butadiene. Further distillation gives the purified product. Impurities gradually build up due to the degradation of the ACN solvent. They are removed by taking a bleed from the circulating solvent and diluting it with water. Any polymers separate as an oil in a coalescer. Acetamide and ammonia are removed in a solvent recovery column by distillation. Recovered ACN is recycled.

##### Releases to Air

- Acetonitrile, hydrocarbons and ammonia from reactor vents, solvent recovery column vents and during plant decommissioning for maintenance.
- Acetamide from solvent recovery column vents.

##### Releases to water

- Ammonia and acetamide discharged with solvent recovery waste waters, and acetonitrile in process waste waters.
- Sodium nitrite and sodium nitrate in deoxygenation waste waters.

##### Releases to land

- Polymers as a solid waste from the distillation process.

##### (c) The NMP process

In the NMP process, counter-current extraction of the feedstock produces a pure butenes stream and a pure butadiene stream. The solvent is regenerated on a continuous basis in vacuum evaporation vessels to remove polymeric solids. Acetylenes and

C<sub>5</sub> hydrocarbons are removed by distillation, with sodium nitrite added as a scavenger to inhibit polymer formation.

#### Releases to air

- Hydrocarbons from reactor and storage tank vents and during process plant decommissioning for maintenance.

#### Releases to water

- n-methylpyrrolidone and sodium nitrite are lost to water in process purges.

#### Releases to land

- Residue sludge is formed from the regeneration of spent n-methylpyrrolidone, which contains NMP, NMP polymers, sodium nitrate and butadiene.

### 2.2.2 Cumene

Cumene is produced from a reaction between propylene and benzene. The propylene feedstock contains propane as an inert. The reaction is carried out under pressure at 250°C and catalysed by phosphoric acid on kieselguhr. Excess benzene is used to ensure complete conversion of the propylene. Products are separated by distillation, where propane is removed. Higher alkylated benzene by-products may be converted to cumene by transalkylation with additional benzene. Unreacted benzene is recycled to the reactor.

#### Releases to air

- From storage tank blanket gases.
- Purge and let-down gases are generally routed to flare,

thereby releasing oxides of carbon.

#### Releases to water

- Phosphoric acid, hydrocarbons and amines from acid pot drainings and decommissioning washes.

#### Releases to land

- Spent catalyst and process residues.

### 2.2.3 Ethanol

Most industrial ethanol is manufactured by the vapour-phase hydration of ethylene over a solid catalyst. Ethylene and water vapour are passed over a phosphoric acid catalyst supported on porous clay beads at around 240°C and 68 barg. The reactor product is scrubbed with water to separate the ethanol. Unreacted ethylene is recycled. Ethanol is obtained from its aqueous solution by a series of distillations, followed by azeotropic distillation with benzene.

#### Releases to air

- Hydrocarbons from process vents.

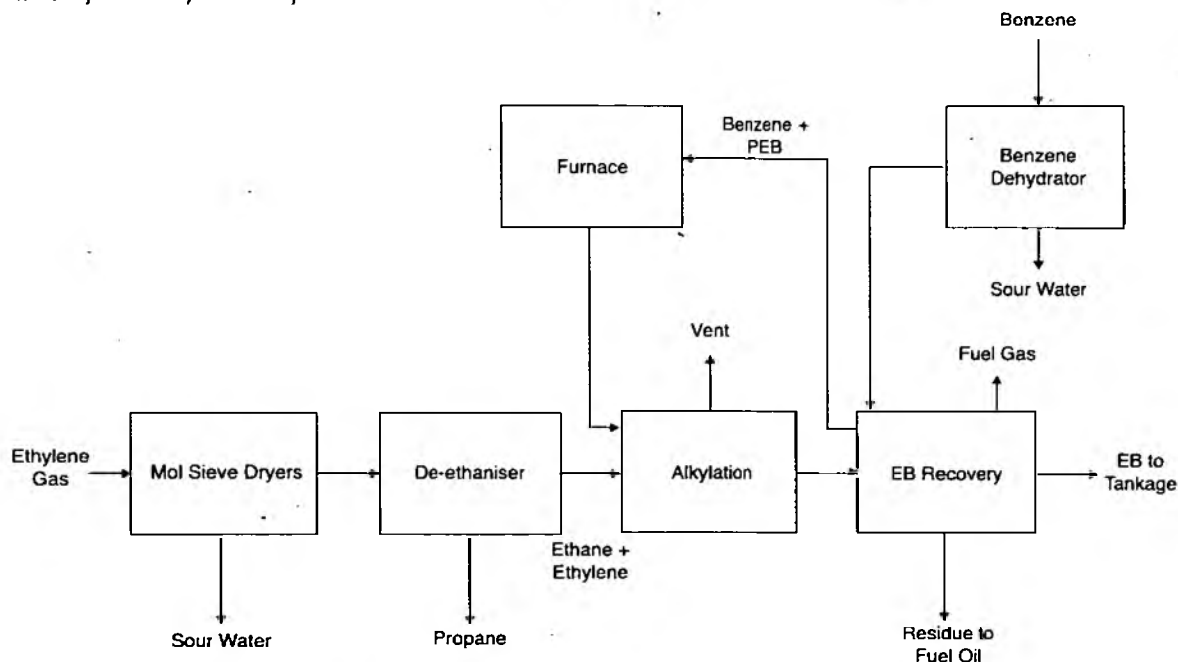
#### Releases to water

- Caustic effluent from washing of the aqueous product prior to distillation and phosphates from the distillation process.

#### Releases to land

- Organic solvents, phosphoric acid and phosphates from spent catalyst.

Figure 2.1 Simplified ethylbenzene production





## 2.2.4 Ethylbenzene

Ethylbenzene is produced by the vapour-phase alkylation of benzene with ethylene over a proprietary zeolite catalyst (Figure 2.1). Both reactants are pre-dried. The product is isolated by successive distillation stages to remove benzene, which is recycled to the feed, and polyethylbenzene, which is returned to the reactor. Impurities such as methane, hydrogen and ethane are separated from the reactor products and routed to the refinery fuel gas system. Pre-drying is by molecular sieves, which are regenerated using process gas at 220°C. The zeolite catalyst is regenerated by burn-off using recirculated nitrogen containing 0.6 to 0.7% oxygen. A bleed of gas is vented to atmosphere to remove the resultant carbon dioxide.

### Releases to air

- Oxides of carbon and oxides of nitrogen from catalyst regeneration.
- ⊙ Losses of benzene and other compounds from tank vents and loading operations.
- ⊙ Fugitive losses of ethylene, benzene and ethylbenzene from equipment and fittings.

### Releases to water

- Benzene in the dehydration water and hydrocarbons in steam condensate.

### Releases to land

- Spent molecular sieve material.

Special control techniques: double mechanical seals on pumps, containment of benzene vapours from tanks and loading (see Section 3) and stripping of organics from waste water.

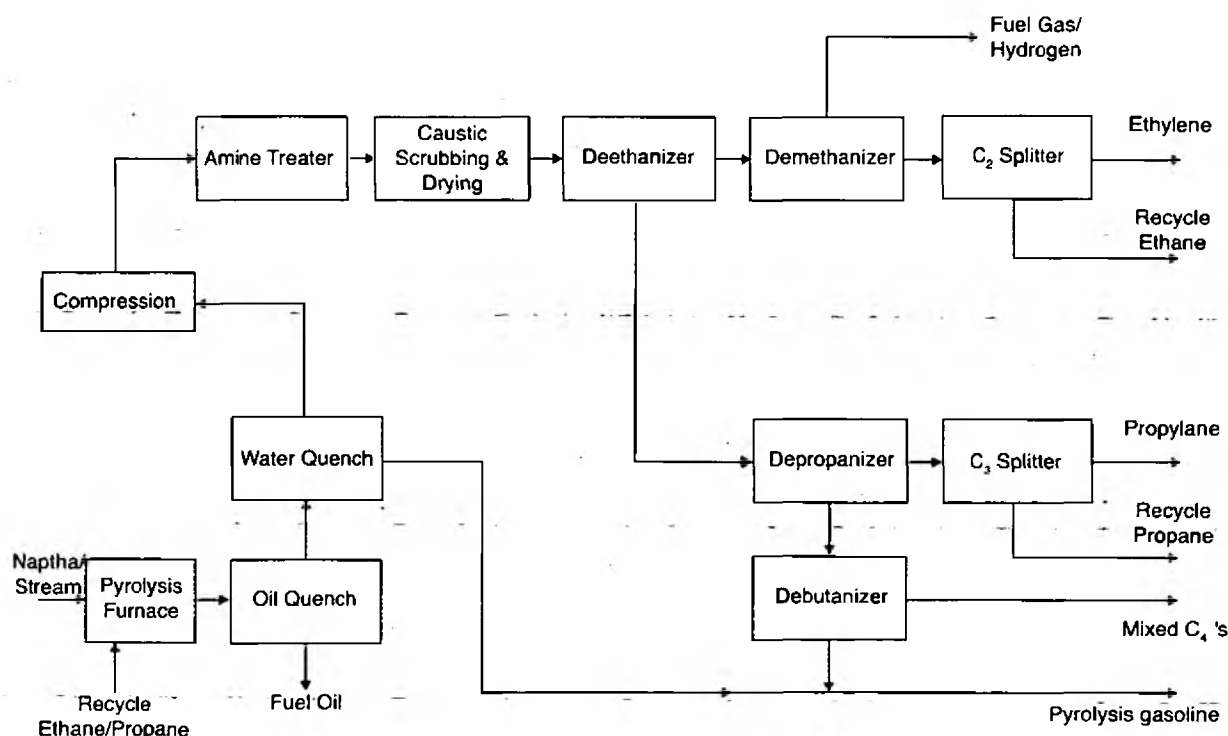
## 2.2.5 Ethylene/propylene

Ethylene is produced by the steam pyrolysis of a gaseous or liquid hydrocarbon feedstock, eg ethane, naphtha and gas oil (Figure 2.2). Mixed co-products are also produced, including higher alkenes (olefins) such as butadiene and pentenes. Some reforming can also occur, providing an aromatic-rich co-product stream, commonly known as pyrolysis gasoline. The quantity of by-products produced increases as the feedstock molecular weight increases. For example, cracking of ethane will produce virtually no co-products whilst cracking of naphtha will yield a broad range of co-products, including propylene.

Feedstock and steam are subjected to high-temperature cracking and the resultant gas is cooled in steam-generating facilities and may be oil-quenched. Further cooling in the pyrolysis fractionator results in fuel oil and some gasoline components separating from the main gas stream. The remaining gases are cooled, compressed, and subjected to acid gas removal and dried prior to cryogenic demethanisation. A methane-rich fuel gas stream and an ethylene ethane fraction are recovered. The latter is further fractionated to produce polymer-grade ethylene as well as ethane, which is recycled. Propylene and heavier components are separated by fractionation.

Ethylene crackers tend to be very large plants, processing small molecules at moderate pressure, hence fugitive emissions of feedstocks and products can be significant. Start-up and shut-down of the process places heavy demands on environmental systems, particularly the flare.

Figure 2.2 Ethylene process: steam cracking of naphtha



**Releases to air**

- Oxides of carbon and oxides of nitrogen from incineration waste gases, regeneration heaters and acetylene reactor regeneration.
- Hydrocarbons from flares (start-up, shut-down and process upsets).
- Fugitive releases, ie particulates and combustion products resulting from decoking operations.

Special control techniques: optimisation of furnace design to minimise coking; high-integrity equipment and fittings on gas and volatile liquid duties; fugitive emission reduction scheme; good operating procedures to minimise flaring at start-up and shut-down.

**Releases to water**

- Polymer from sludge dewatering.
- Zinc/chromium and zinc/phosphorus formulations, hypochlorite and sulphuric acid from cooling tower blow-down.
- Process condensate from a drying process and spent caustic from acid gas removal.
- Soluble hydrocarbon oils from process purges.

**Releases to land**

- Butadiene polymers from depropaniser waste.

- Ash and heavy hydrocarbons from oil/water separator sludge.
- Spent catalyst from the reactor.

**2.2.6 Ethylene glycol**

Ethylene glycol (MEG) is produced from ethylene oxide and water. Higher glycols are produced as by-products, the most significant being diethylene glycol (DEG). The ethylene oxide is mixed with excess water and hydrolysed at above 190°C. The ethylene glycol is purified by distillation with recycling to improve recovery. Further ethoxylation of the DEG yields tri- and tetraethylene glycol.

A combined ethylene oxide and ethylene glycol plant is shown in Figure 2.3.

**Releases to air**

- Vents and purges from process streams.

**Releases to water**

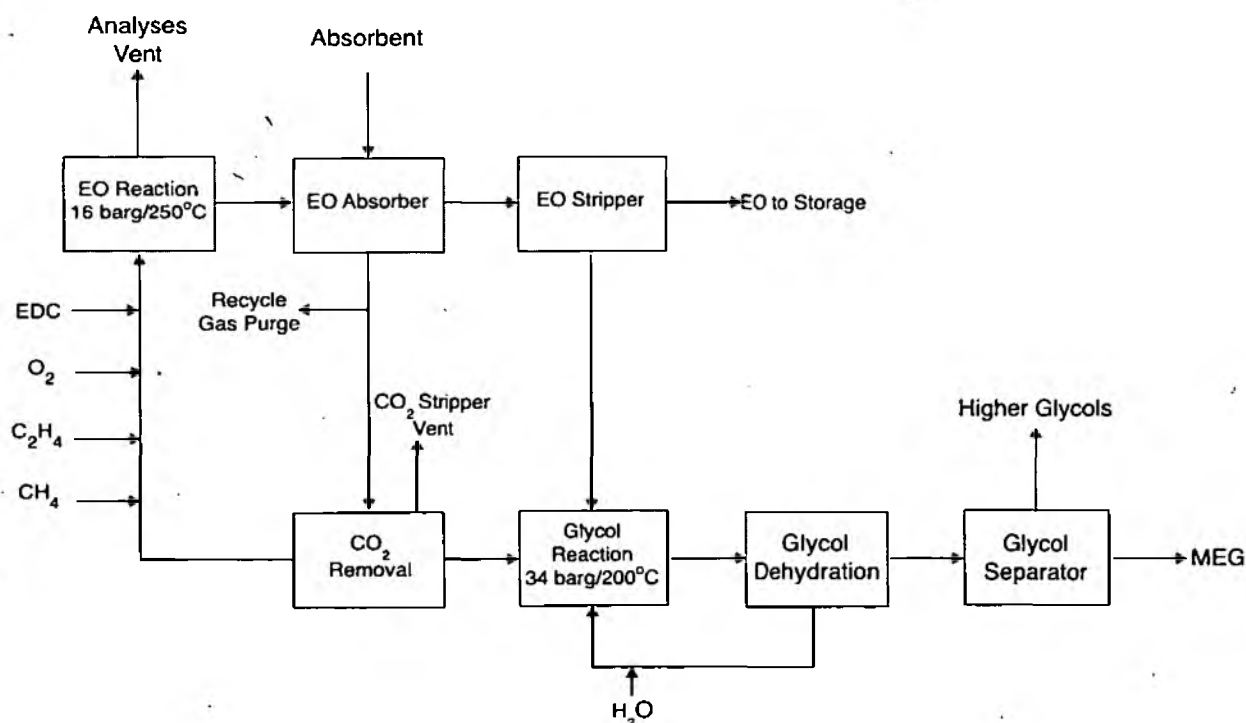
- Glycols may be released in ejector condensate and purge streams.

**Releases to land**

- None.

Special control techniques: minimisation of water purges by recycling.

**Figure 2.3 Ethylene oxide/ethylene glycol production**



### 2.2.7 Ethylene oxide

Ethylene oxide (EO) is manufactured by the oxidation of ethylene over a silver-based catalyst. Although ethylene oxide can be produced by an air-based process, most modern processes are oxygen-based. The reaction at 250°C is exothermic, with the heat of reaction being removed by raising steam. The reactor effluent is cooled, passed to an absorber and the quenched gas contacted with water to recover the products as a dilute aqueous solution. This solution is heated and the product separated by steam stripping. Unreacted ethylene is recycled to the reactor and the by-product ethylene glycol is fed directly to an ethylene glycol plant. Ethylene oxide is purified by distillation. Part of the recycled gas (about 20%) is treated to remove significant quantities of carbon dioxide, generated in the oxidation process, before return to the reactor.

#### Releases to air

- Oxides of carbon and hydrocarbons from loop purges and the carbon dioxide absorber vent.
- Ethylene oxide from the reactor analyser vents, the purification process and storage vents.
- Small amounts of ethylene dichloride, which is used in small quantities to modify the oxidation reaction, are also released.

Special control techniques: flash unit to recover hydrocarbons from the CO<sub>2</sub> absorber liquors; refrigerate EO storage; ground level flare for the reactor purge loop.

#### Releases to water

- Ethylene glycol from ethylene oxide quench purges and carbon dioxide absorber purges.
- Sodium salts from ethylene oxide quench purges; potassium salts from carbon dioxide scrubber purges.
- Aldehydes from aldehyde purges.

#### Releases to land

- None.

### 2.2.8 Higher olefins

Higher olefins are linear olefins (alpha and internal) in the carbon range C<sub>6</sub> to C<sub>20</sub>. The product from the higher olefin process depends on both the process technology and the feedstock. Ethylene and propylene/butene feedstocks are used in the UK. The process consists of two complementary techniques:

- oligomerisation for synthesis of alpha olefins from ethylene; and
- isomerisation/disproportionation for conversion of light and heavy alpha-olefins to internal olefins.

Oligomerisation is catalysed by a metal ligand catalyst dissolved in a solvent that is largely immiscible with the alpha olefin product. A three-phase mixture solvent containing catalyst, oligomer product and ethylene gas is circulated through a series of reactors. The heat of reaction is removed by water-cooled exchangers. As product is formed it separates from the solvent catalyst phase and enters the hydrocarbon phase. The product is separated from the catalyst solution and ethylene, which are recycled; the product is scrubbed with solvent to remove catalyst.

Dissolved ethylene in the product is recovered by distillation for recycle. The product is then distilled to recover individual olefins and by-products, which are fed to the second reaction stage of isomerisation/disproportionation. The reactors are operated at 80-120°C and 68-136 barg. Reaction rate is controlled by the rate of catalyst addition.

Ethylene is converted to a range of alpha olefins of even carbon number by an oligomerisation reaction.

In the second process step light C<sub>4</sub> olefins and C<sub>20+</sub> olefins (plus unwanted C<sub>6</sub> - C<sub>18</sub> olefins) are converted to mid-range C<sub>6</sub> - C<sub>14</sub> internal olefins by molecular rearrangement. The double-bond is shifted away from the alpha position to any of the internal positions.

Isomerisation/disproportionation is carried out at 80-140°C and 4-7 barg, with negligible heat generation. Feedstocks are first purified to remove alpha olefins, catalyst and solvent residues. Double-bond isomerisation of the alpha olefins and disproportionation are controlled by separate catalyst systems. The desired products are separated from the resulting reaction mixture by distillation and unwanted fractions are recycled. Impurities are removed in process bleed streams.

#### Releases to air

- Oxides of carbon and oxides of nitrogen from on-site incinerators.
- Hydrocarbons from storage tank vents and the incineration of tank bottoms.
- Nickel from incineration of interceptor sludge and catalyst.
- Aluminium oxide from incineration of isomerisation catalyst.

#### Releases to water

- Nickel compounds from aqueous interceptor discharge.

#### Releases to land

- Cobalt and molybdenum from spent catalyst.

### 2.2.9 Isopropyl alcohol

There are two distinct methods for manufacturing isopropyl alcohol:

- indirect hydration of propylene using sulphuric acid as a homogeneous catalyst; and
- direct hydration of propylene using a heterogeneous catalyst this reaction may take place in the vapour phase, the liquid phase or a vapour liquid mixture.

Each process and its major effluents and wastes is described below.

#### (a) The indirect hydration process

This process produces isopropyl alcohol and four other solvents (diisopropyl ether, dimethyl ketone, secondary butyl alcohol, and methyl ethyl ketone). Propylene and butylenes in mixed C<sub>3</sub> streams and mixed C<sub>4</sub> streams are reacted with 70–75% sulphuric acid to form the corresponding alkyl sulphates, which are subsequently hydrolysed to the corresponding alcohols. The related ethers are formed as by-products.

The crude alcohols are purified by distillation to give an isopropyl alcohol azeotrope with water and relatively pure secondary butyl alcohol. These may be sold or converted to the related ketones by dehydrogenation over a brass catalyst.

##### *Releases to air*

- Oxides of carbon, oxides of nitrogen and oxides of sulphur from the incineration of waste process gases.
- Hydrocarbons from tank vents, strippers, condensers and reaction time tanks.
- Isopropyl alcohol from the cooling tower.
- Chromium from the incineration of solvent slugs.
- Nickel from the incineration of caustic sludge.

##### *Releases to water*

- Alcohols, ketones, furfural, copper and zinc from aqueous interceptor discharges, spent sulphuric acid and caustic soda.

##### *Releases to land*

- Spent brass catalyst if not regenerated.
- Ash from incinerator.

#### (b) The direct hydration process

The propylene feed is purified first by distillation to remove propane. Propylene is then hydrated in the vapour phase.

The major by-product is diisopropyl ether; other by-products include n-propanol, acetone, hexanol and low-molecular-weight polymer. The reaction takes place at approximately 180°C and 34 barg over a catalyst of 42–46% phosphoric acid on porous clay beads.

The product is water-scrubbed to separate the isopropyl alcohol. Unreacted propylene is recycled, a purge being taken to prevent propane build-up. Isopropyl alcohol is purified by distillation, finally azeotropically using cyclohexane as an entrainer.

##### *Releases to air*

- Hydrocarbons from tank and process vents and fugitive releases of hydrocarbons.

##### *Releases to water*

- Propanols, organic phosphates and inorganic phosphates from water wash.

##### *Releases to land*

- Phosphoric acid and phosphates as spent catalyst.

### 2.2.10 Oxo alcohols

Oxo alcohols range from butanols (C<sub>4</sub>) to C<sub>20</sub> alcohols. There are two basic variations to the manufacturing process, one based upon hydroformylation and the other upon carbonylation followed by hydrogenation.

#### (a) Hydroformylation

Synthesis gas, used as one of the feed materials for this process route, may be produced by reforming naphtha or natural gas. Liquid naphtha is desulphurised by hydrogenation at 400°C and 20 barg over a nickel catalyst and the hydrogen sulphide thus formed removed on iron oxide/zinc oxide absorbers. The treated naphtha is then mixed with steam and recycled carbon dioxide and fed to a reformer, for treatment at 850°C and 17.5 barg over a nickel-based catalyst. Carbon monoxide and hydrogen are produced in an endothermic reaction, with carbon dioxide and methane as by-products. Part of the product stream is scrubbed to remove carbon dioxide.

For normal butyl alcohol manufacture, synthesis gas is fed, with propylene and catalyst to a reactor system. After reaction at 170°C and 70 barg, gases, mainly unreacted propylene and synthesis gas, are removed to leave a mixture of catalyst in alcohol, which is then distilled to produce a crude normal butyl alcohol. This is purified by distillation and azeotropic distillation to separate isobutyl alcohol from the product.

C<sub>7</sub>–C<sub>15</sub> alcohols are produced from the respective olefins by combination with synthesis gas. The reaction takes place at 180 to 200°C and 50 barg over catalyst. After depressuring and recycling of evolved gas, the crude product is distilled under vacuum. The crude alcohol is treated with caustic soda to saponify by-product formates, water-washed and

then distilled to remove unreacted olefins, by-product paraffin hydrocarbons and heavy fractions. Finally, the alcohols are hydrogenated at elevated temperature and pressure over a nickel catalyst to remove the last traces of aldehydes.

#### *Releases to air*

- Oxides of carbon, oxides of nitrogen and oxides of sulphur from the incineration of process waste gases and plant ejector vents.
- n-Butanol and mixed hydrocarbons from plant ejector vents and sludge incineration.

#### *Releases to water*

- Suspended solids, butanols, aldehydes and butyl formate from contaminated process aqueous effluent.

#### *Releases to land*

- Zinc oxide, cobalt, molybdenum, chromium oxide, iron oxide, copper oxide and activated carbon from the desulphurisation and converter catalysts and activated carbon absorbers.

### **(b) Carbonylation and hydrogenation**

The liquid olefins are reacted with carbon monoxide and hydrogen in the correct proportions at 145°C and 260-270 barg to give liquid aldehydes, and by-products including heavy ends resulting from aldehyde side-reactions. After separation from the carbon monoxide and hydrogen, which are recycled, the aldehydes are vaporised with hydrogen and hydrogenated to give the corresponding alcohol. The alcohol is cooled, separated from the hydrogen and purified. Purification is by distillation to remove unreacted olefins, methanol, water and heavy ends.

#### *Releases to air*

- Oxides of carbon from the catalyst let-down vessels and reactor blow-down.
- Alcohols from hydrotreater vents.

#### *Releases to water*

- Hydrocarbons in ejector condensate.
- Methanol in wash waters.

#### *Releases to land*

- Spent catalyst.

### **2.2.11 Vinyl acetate**

Vinyl acetate can be produced from acetylene and acetic acid. In the UK, vinyl acetate is produced only from ethylene, acetic acid and oxygen. Carbon dioxide, water, acetaldehyde, ethyl

acetate and higher esters are formed as by-products. The reaction takes place in the vapour phase at 160°C and 8 barg over a noble metal catalyst of palladium and gold and potassium acetate supported on silica beads. The product is quenched, carbon dioxide is removed using hot potassium carbonate, and unconverted oxygen and ethylene recycled. A purge stream prevents inert build-up. Unconverted acetic acid is separated from the crude product by distillation and recycled. The vinyl acetate is purified in a series of distillation columns.

#### *Releases to air*

- Hydrocarbons from the reactor loop purge.
- Carbon dioxide from the absorption/desorption system.

#### *Releases to water*

- Sodium acetate in the neutralised aqueous effluent from water stripping.

#### *Releases to land*

- None (assuming high boilers, light ends, etc are used as fuel).

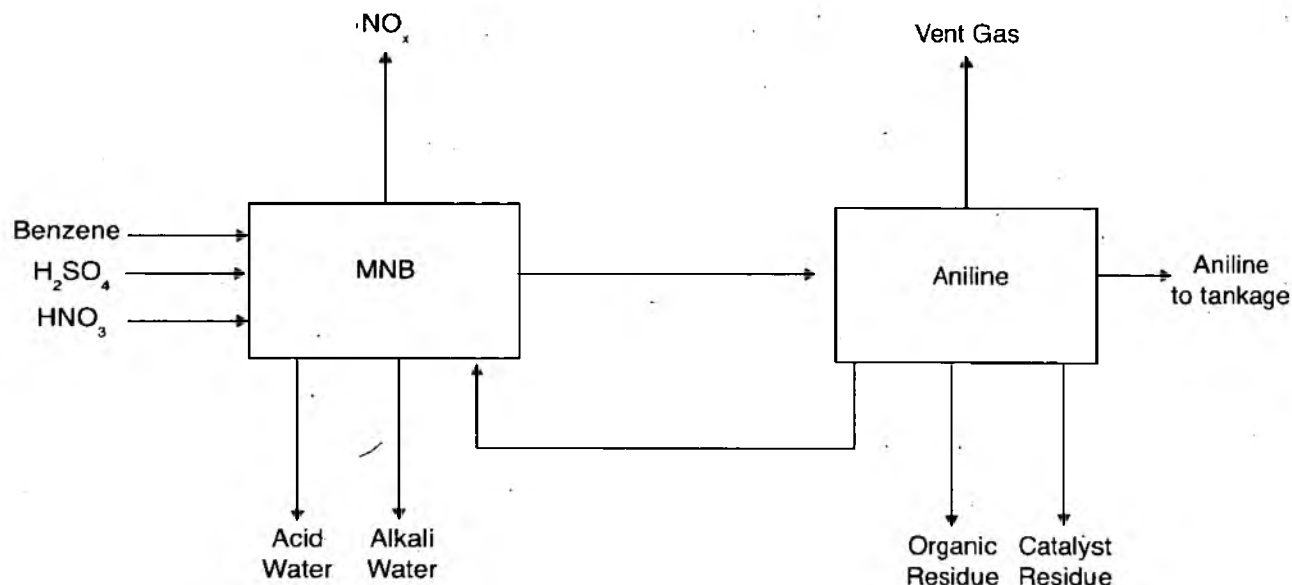
### **2.2.12 Chlorinated hydrocarbons**

Chlorination reactions are covered in IPC Guidance Note<sup>(9)</sup> S2 4.02 as most are batch processes. In large-scale plants an organic feedstock is reacted with halogen or halide in a pressurised continuous reactor at elevated temperature in the presence of a catalyst. A range of halogenated organic products is formed, which are separated by condensation and distillation in a train of columns depending on the complexity of the mixture. Unwanted by-products are recycled to the process where possible. Unreacted halogen and halide should be recovered and returned to the process or other productive use wherever practicable. Where it is necessary to vent a gas stream, releases of chlorinated hydrocarbons and other VOCs should be minimised by the techniques detailed in Section 3. Emergency vents should be directed to a collection system with suitable abatement facilities.

Examples of these processes include the reaction of ethylene and chlorine to form ethylene dichloride and its subsequent conversion to vinyl chloride, which is described in Section 2.6.2. Ethylene dichloride can be further chlorinated in the presence of oxygen to trichloroethylene and perchloroethylene. The hydrochlorination of methanol yields methyl chloride, which can be further chlorinated to methylene chloride.

Hydrochlorofluorocarbons are made by the hydrofluorination of chlorocarbons such as chloroform. By-products include some hydrofluorocarbons, which have high global warming- and ozone depletion potentials. In the absence of productive use, they should be incinerated with scrubbing of the resulting gases and not released to the environment. Residues such as heavy ends from distillations should be incinerated and not released to land.

Figure 2.4 Potential emissions on simplified nitrobenzene/aniline process



## 2.3 Nitrogen compounds

### 2.3.1 Introduction

Production units for these chemicals range from large dedicated petrochemical-type facilities to small multi-purpose chemical plants, which are run on a campaign basis. The characteristics of batch processes are described in IPCGN S2 4.02<sup>(8)</sup>. The manufacture of isocyanates is covered in CIGN 6/4<sup>(22)</sup>.

### 2.3.2 Aniline

Aniline is produced commercially worldwide either by the reduction of nitrobenzene (the Bechamp process) or by the catalytic hydrogenation of nitrobenzene.

Catalytic hydrogenation can be carried out in either the gaseous or liquid phase and the gaseous route either uses a fixed-bed or a fluidised-bed catalytic reactor. The production of nitrobenzene and aniline are often integrated, as in the UK. The following description applies to the combined facility. A typical flowsheet is shown in Figure 2.4.

Benzene is converted to mononitrobenzene (MNB) in a mixture of nitric and sulphuric acids in a conventional stirred tank reactor at approximately 70 °C. Benzene is converted to MNB at a selectivity of around 97%. Effluent from the reactor is decanted into a separator where crude MNB is separated from the acid solution. This acid solution is concentrated by steam stripping and recycled back to the reactor. Crude MNB is washed, vaporised, and fed to a fluid-bed reactor containing a copper silica catalyst. Reactor effluent passes to a separator where two phases form. The organic phase contains water and is fractionated in a tower to retain aniline. The aqueous layer contains some aniline and typically is sent to the site waste-water system. The main waste-water sources are the crude nitrobenzene wash-water and aniline water formed in the final separator.

#### Releases to air

- NO<sub>x</sub> emissions from nitrobenzene are often controlled by caustic scrubbing prior to discharge to atmosphere.
- Vent gases (mainly methane and hydrogen) have a high calorific value and can be sent to the site fuel gas header main according to site layout or, alternatively, are burnt.

#### Releases to water

- Nitrobenzene has two liquid effluents: alkali water, which represents a major pollutant, and acidic water. The acidic water stream is usually managed in a conventional bio-treatment plant after neutralisation.
- Alkali water (sometimes known as "red water") is particularly toxic and contains toxins such as nitrophenols and picrates. These toxins pass from the organic phase to the aqueous phase during washing. Typical concentrations range from 1000 to 10000 ppm. Various abatement techniques have been employed including wet air oxidation, incineration and charcoal adsorption followed by incineration.

#### Releases to land

- Catalyst residues (copper/silica) are either disposed of by landfill or recycled.

### 2.3.3 Uses of aniline

#### (a) Cyclohexylamine

Cyclohexylamine is produced by the liquid-phase hydrogenation of aniline in the presence of a catalyst such as cobalt, nickel or ruthenium/palladium.



Aniline and hydrogen are reacted continuously to produce cyclohexylamine. Typical reactor conditions are 9 barg and 210°C although high-pressure processes (60 barg and 230°C) can also be used.

Depending upon the end-use of the cyclohexylamine, purification may not be necessary and is not required in the UK. Cyclohexylamine is usually stored under a nitrogen blanket.

Waste streams arising from cyclohexylamine production come from the reactor purge gases (feedstock hydrogen usually contains methane, which must be removed periodically from the reactor), and from spent catalyst removal. Owing to the high metals value of the catalyst, reprocessing of spent catalyst is often carried out.

### (b) Mercaptobenzothiazole

For details of the manufacture of mercaptobenzothiazole, reference should be made to Section 2.7.

### 2.3.4 Methylamines

The three methylamines, monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA), are all produced in equilibrium in the catalysed vapour-phase alkylation reaction of ammonia with methanol, which is carried out at elevated temperature and pressure (Figure 2.5).

The same basic process is used worldwide and consists of a fixed-bed reactor followed by a distillation purification train. Variations occur in the catalyst type used and also in the distillation train arrangement, with three main different configurations being used worldwide.

The alkylation of ammonia with methanol is carried out at 260–320°C and a pressure greater than 20 barg. Conventional dehydration catalysts are commonly used.

Ammonia and methanol are fed as a vapour into the primary circuit, which normally consists of a series of reactors with interstage cooling containing a DMA selective dehydration catalyst. The secondary circuit is then configured, to promote the equilibrium either to TMA or to DMA from TMA as required, by changing the operating conditions in the reactor.

The product stream is distilled to separate the products from the ammonia. The initial column recovers ammonia, which can be returned to bulk storage. The gaseous phase from the second column is returned to the reactor inlet. The bottoms from this column is 'crude' product and consist of MMA, DMA, TMA, unreacted methanol and water.

This crude product stream can then be distilled into its various components. Three product streams of MMA, DMA and TMA are produced, which can be sent to the relevant storage facilities or to the secondary reaction circuit as required.

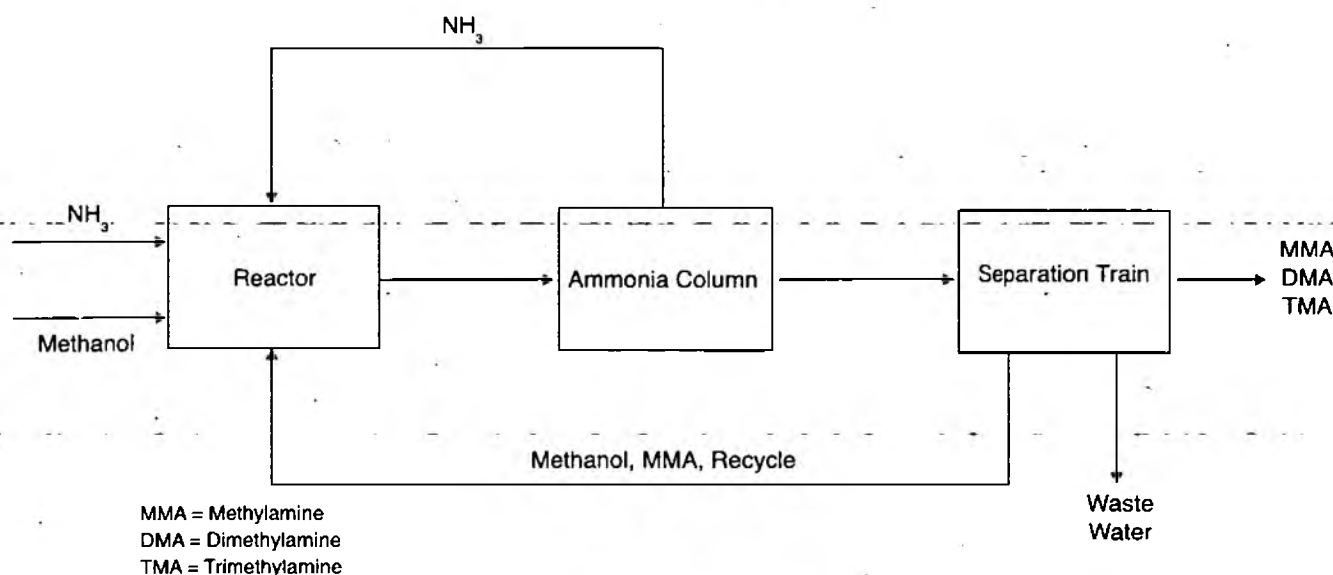
The methanol stream is purified and recycled to the reactor inlet. An aqueous stream with associated organic impurities for disposal is also generated.

#### Releases to air

- Process vents that contain methylamines should be routed via an absorption system in order to prevent releases. Any absorbed amines can then be recovered in a stripper and recycled within the process, thus minimising losses.
- Owing to the low odour threshold of MMA, DMA and TMA, it is important that leaks are minimised. This includes the design of storage and handling facilities, seals on pumps, and the minimisation of flanges in pipework.

Special control techniques: releases to air are minimised by scrubbing towers and absorbers. If necessary to remove odour,

Figure 2.5 Manufacture of methylamines



appropriate back-up systems may include bio-treatment or incineration.

### *Releases to water*

- Waste water generated in the reaction of methanol and ammonia plus scrubber water purges. All contain soluble amines and ammonia.

Special control techniques: minimisation of water usage in the scrubbing systems; biological treatment of waste water.

### *Releases to land*

- Another waste stream resulting from the process arises from the periodic replacement of the catalyst in the reactors.

## **2.3.5 Uses of methylamines**

### **(a) Aminoethanols**

In the UK dimethylaminoethanol (DMAE) is produced commercially by the methylation of ethylene oxide in the presence of a ruthenium catalyst at elevated temperature and pressure. By-products of the reaction result from the presence of trimethylamine impurities in the feedstock and from reactions between product DMAE and ethylene oxide to produce high-molecular-weight impurities.

In the reaction section an excess of dimethylamine is maintained in order to ensure the complete conversion of the ethylene oxide feedstock. The reaction is highly exothermic.

A suitable reaction system consists of a loop reactor operated at a high recirculation rate and from which product can be continuously removed and fresh feedstocks and recycled dimethylamine continuously added. This system allows good control of temperature and of the rate of addition of the reactants, both of which are critical to maintain high DMAE yield and minimise the formation of by-products.

The 'crude' reaction product contains excess dimethylamine, which is stripped out under reduced pressure, condensed and recycled to the reactor inlet. Temperature control of the stripper is required to prevent product DMAE being carried over in the overheads and being recycled to the reactor, where it would react further to produce impurities.

The crude product is vacuum distilled to separate light ends and DMAE from the heavy residues. The heavy residues contain DMAE, some of which is recoverable by further distillation before the residues are sent for disposal. The overheads DMAE stream is condensed before storage.

Vents from the reactor section, stripper unit and final distillation stage and other sources likely to contain dimethylamine may be collected together and vented via an acid scrubber. This would generate a waste acid stream for disposal.

### **(b) Dimethylcyclohexylamine**

Dimethylcyclohexylamine (DMCHA) is produced commercially from the reaction between cyclohexanone, dimethylamine and hydrogen. An alternative route involving the ammonolysis of dimethylcyclohexanol (Halcon process) is not currently used commercially.

There are two basic reaction steps involved in the production of DMCHA. The first involves the reaction between cyclohexanone and excess dimethylamine at elevated temperature and pressure to produce an imine. Any hydrogen present will react with cyclohexanone to produce cyclohexanol. The imine is then hydrogenated in the presence of a heavy-metal catalyst at elevated temperature and pressure to give the product DMCHA.

It is usual to carry out both stages of the reaction in a single agitated reactor. Completion of the second stage of the reaction is indicated by a fall-off in hydrogen uptake. Excess hydrogen is normally flared.

Heavy-metal catalyst is reclaimed by filtration of the crude reactor product.

The DMCHA is distilled off from the excess dimethylamine and water of reaction in a two-stage system. Dimethylamine is removed in the overheads from the first column, condensed and returned to the reactor.

Vents from the condenser unit and other facilities on the plant will contain appreciable quantities of dimethylamine, which must be removed prior to discharge to atmosphere.

The bottoms product is crudely separated in a phase separator, producing an aqueous waste stream and then batch vacuum distilled. The water/light ends fraction is phase-separated and the aqueous phase sent for disposal and the light ends recycled. Heavy ends residue will remain at the base of the column for subsequent disposal.

Minimisation of gaseous releases from the plant is of great importance and the collection and scrubbing of all process vents and reliefs should be undertaken. Gaseous releases are scrubbed in order to absorb the amines. This produces an amine-contaminated aqueous effluent from the scrubber for disposal or recycle.

### **(c) Dimethylformamide**

Dimethylformamide (DMF) is produced by the highly exothermic reaction between dimethylamine and carbon monoxide carried out in the liquid phase at elevated temperature and pressure in the presence of a sodium methoxide catalyst/solvent.

If a pure carbon monoxide feedstock is available then unreacted carbon monoxide and the excess dimethylamine present in the reactor off-gases can be separated from the product and catalyst system and recirculated back to the reactor inlet.

At the end of the reaction, water is added to the reactor to deactivate the catalyst. The reactor product mix consists of the crude product and the catalyst/solvent. Various configurations of distillation/separation system are available, all of which produce an unreacted dimethylamine stream, which can be recycled, a product DMF stream and an aqueous waste stream. This can be treated by evaporative techniques to produce an aqueous phase and a solid waste stream for disposal.

A vent system collects all process vents and reliefs together and routes them to a flare system, if hydrogen is present, or to a suitable scrubbing system if the carbon monoxide feed is pure. In either method odorous dimethylamine releases should be prevented.

The process is heavily fouling of heat transfer surfaces and regular cleaning is required, which will generate significant quantities of aqueous effluent.

#### (d) Dimethylacetamide

Dimethylacetamide (DMAC) is produced by the highly exothermic reaction between dimethylamine and methyl acetate carried out in the liquid phase at elevated temperature and pressure and in the presence of a sodium methoxide catalyst/solvent.

The production of DMAC is usually carried out in the same production facilities used for dimethylformamide (DMF). (See Section 2.3.5(c) above for details.) The basic difference is the quantity and composition of the effluent discharges. DMAC production leads to the production of more solid waste for disposal but in all other aspects the systems are similar.

#### (e) Choline chloride

Choline chloride is manufactured by a two-stage batch process involving hydrochlorination followed by ethoxylation of trimethylamine. The first step involves neutralisation of trimethylamine with dilute hydrochloric acid to form a salt. This is carried out at atmospheric pressure and at a slightly elevated temperature (30–50°C). In the second stage this salt is then ethoxylated using ethylene oxide to give choline chloride.

There are two major side-reactions that are liable to occur: ethylene oxide with water, and ethylene oxide with hydrochloric acid unreacted from the neutralisation stage. These reactions produce monoethylene glycol and ethylene chlorohydrin respectively.

The acidic vapours resulting from the reaction section are routed to a scrubber before release to atmosphere.

The crude product can be purified by stripping under vacuum, separating the water associated with the hydrochloric acid feedstock from the choline chloride product. Contaminated water is removed as overheads and can be condensed and sent for disposal.

### 2.3.6 Quaternary ammonium salts

Quaternary ammonium salts (general formula  $R_4N^+X^-$  where X is typically a halide ion; R is an aliphatic or aromatic group) are formed by the alkylation of amines. Amines react with an alkyl halide to form the next higher amine in the series and the reaction can proceed to the final stage to produce the quaternary salt.

In the UK trimethylamine (TMA) is reacted with dichloroethane (DCE) to produce the chlorinated quaternary salt as an aqueous solution.

The process involves the batch reaction of the two liquid feeds, with the DCE present in excess, carried out at 2.5 barg and 100°C. The reaction is exothermic and is controlled by carefully monitoring the addition of TMA and rate of heat removal.

Upon completion of the reaction, water is added to form an aqueous product phase and a DCE organic phase. The DCE phase can be separated and recycled to the reactor whilst the remaining aqueous phase must be heated to generate the DCE/water azeotrope. This can be condensed and recycled.

The pH of the aqueous product phase, stripped of volatile amine and DCE, is adjusted and the product stored.

Processes that use DCE are subject to EC Directive 90/415/EEC(15):

### 2.3.7 Ethylamines/isopropylamines

Ethylamines and isopropylamines are usually produced on the same plant on a campaign basis. The basic reactor system design is used worldwide with variations on the associated distillation system. Primary, secondary and tertiary ethylamines are produced concurrently but the formation of the tertiary isopropylamine is inhibited by steric effects. The manufacture of the various products is governed by the relative market demands and consequently the ability to recycle surplus product is required. Diethylamine is generally the most important product.

Ethylamines/isopropylamines are manufactured from the reaction between anhydrous ammonia and either ethanol or isopropanol. The reaction is carried out in the gas phase at elevated temperature and pressure in the presence of a hydrogenation catalyst, eg Raney nickel.

Modern catalysts ensure essentially complete conversion of all the alcohol so that the requirement for azeotropic distillation and alcohol recovery columns, as installed on older plants, no longer exists. Hydrogen is usually recirculated via a condenser and gas separator to suppress the formation of reaction impurities, and excess heat is removed to prevent degradation of the catalyst.

Ammonia is first removed as an overhead, recycled and then distilled to separate the mono-, di- and triethylamine streams from an aqueous waste stream.

The aqueous phase will contain amines and these are reclaimed via a stripping column. Any inerts periodically purged from the system will also have associated amines present, which are removed prior to discharge by an absorber/stripper system.

Periodic catalyst replacement, which is required as performance deteriorates, creates a solid waste catalyst stream, which must be regenerated. As catalyst performance falls, heavy impurities are produced, which are removed in the purification section and sent for disposal.

### 2.3.8 Ethanolamines

Ethanolamines are produced by the exothermic reaction between ethylene oxide and ammonia. All three derivatives, monoethanolamine (MELA), diethanolamine (DELA) and triethanolamine (TELA), are produced concurrently.

The reaction is carried out at an elevated temperature and pressure, with ammonia in excess to ensure complete conversion of the ethylene oxide. The requirement for the presence of a catalyst is dependent upon the reactor operating conditions.

By-product residues are formed but are inhibited by the relatively slow reaction rates.

In response to changing market demands the relative distribution of MELA, DELA and TELA in the crude reactor product stream can be varied. A high ammonia to ethylene oxide ratio is used when MELA and DELA are required, whereas recycling of product MELA and DELA is employed if DELA and TELA are the primary products. However, production of TELA also increases the production of heavy residues.

The crude product stream resulting from the reaction consists of water, excess ammonia, MELA, DELA, TELA and residues. This is separated by a series of distillation stages to provide product-grade components and waste residues. Product TELA normally contains 15% DELA as an impurity. The excess ammonia and the water can be reclaimed and recycled to manufacture ammonia solution suitable for the reactor feedstock.

The initial purification step following the reactor involves the removal and recovery of the excess ammonia from the crude product stream. This is achieved by distillation. This ammonia will generally then be recycled to an on-site recovery system consisting of a scrubbing column in which the recovered water and ammonia are contacted with fresh anhydrous ammonia and make-up water to form a concentrated aqueous ammonia feed.

Amines carried over in the recovery column overheads are usually recycled in this manner although the periodic purging of inerts from the system will tend to release ammonia and amines in small quantities.

Following removal of excess ammonia the water must be removed from the crude product stream, generally by evaporation. Water/amines condensed overhead are used as a reflux to the system and as a feed to the ammonia scrubber.

Purification of the mixed concentrated crude ethanolamines stream is carried out by vacuum distillation.

Water that enters the purification system with the dehydration column bottoms is removed in the column overheads and must be condensed and purged from the system. Some loss of product is associated with this operation.

### 2.3.9 Nitriles and derivatives

#### (a) Acrylonitrile

Acrylonitrile is produced by the vapour-phase ammoxidation of propylene using excess ammonia in the presence of an air-fluidised heavy-metal catalyst. A fixed-bed catalyst system may alternatively be used. Acrylonitrile and water of reaction are formed; hydrogen cyanide, acetonitrile, carbon oxides and other organics (eg acrolein) are formed as by-products. Catalyst efficiencies have increased to over 75%, reducing the quantity of by-products passing to recovery or incineration.

The propylene is usually stored on-site in either a brine cavity or storage sphere and ammonia either in refrigerated storage tanks at atmospheric pressure or under pressure at ambient temperature. Propane is usually present as a significant impurity of the propylene feedstock and must be purged from the system.

The reactor off-gases will contain catalyst fines, and these are reclaimed and returned to the reactor by either cyclones within the reactor or by external cyclones. Fresh catalyst must be continuously added to the reactor to replace losses. The reactor off-gases are quenched to remove the excess ammonia. Owing to other impurities present at this stage the ammonia cannot be recycled and therefore dilute sulphuric acid is used as the quenching medium. The ammonium sulphate is treated and sold as a by-product.

An alternative is to contact the reactor off-gases with a circulating stream of ammonium sulphate. In this system fresh sulphuric acid must be added to keep the system acidic and prevent the explosive polymerisation of both the acrylonitrile and the hydrogen cyanide. Catalyst is also removed in these process units and leaves the system with the ammonium sulphate liquor.

Ammonium sulphate can be removed from the liquor using a forced circulation evaporative crystallisation unit to produce a saleable by-product. A waste liquor stream from the crystallisation process is generated, which contains some ammonium sulphate as well as organics removed in the quench process.

After quenching to remove the excess ammonia the reactor off-gases are normally scrubbed with chilled water. The vent gases from this unit contain mainly nitrogen but also some acrylonitrile, carbon oxides, unreacted oxygen and hydrogen cyanide. In most cases this vent gas is treated by incineration or flameless oxidation.

The absorber liquor is passed to a stripper where the product acrylonitrile and hydrogen cyanide are separated in the overheads from the acetonitrile.

The crude acetonitrile is stripped in a further column and is removed overhead whilst the heavy polymeric compounds present in the base liquors are separated out and concentrated. These heavy polymers are usually incinerated in the presence of a support fuel whilst the liquors can be partially recycled. The remainder of the liquor is treated with formaldehyde to remove any free cyanide prior to disposal.

The acetonitrile can be either incinerated or purified further for sale.

The overheads from the recovery column, which consist of acrylonitrile and hydrogen cyanide, are distilled to produce the two products.

Hydrogen cyanide is either sold (if a market is available) or incinerated. If hydrogen cyanide is stored on-site it is kept under acidic conditions and phosphoric acid, sulphur dioxide and acetic acid are often added to prevent polymerisation from occurring.

Release of acrylonitrile to atmosphere during storage can be significant and storage tanks must be vented to a safe location. In order to protect against possible polymerisation reactions occurring during storage, small quantities of inhibitors are added. One of these, MEHQ (monoethyl ether of hydroquinone), requires small quantities of dissolved oxygen in order to be effective. Tank breathing losses must then be minimised by a suitable method, ie an internal floating roof structure for storage tanks or connection to an incinerator. The high destruction temperature of acrylonitrile, however, may necessitate a support fuel especially if the tank is nitrogen blanketed instead of atmospheric.

Special control techniques: incineration of absorber off-gas; incineration with energy recovery or, preferably, use or sale of hydrogen cyanide co-product; wet air oxidation of waste water from the waste water stripping column, followed by ammonium sulphate recovery; and powdered activated carbon treatment of acrylonitrile stripping and treated waste water stripping column effluents.

## (b) Adiponitrile

Three main processes are used worldwide to manufacture adiponitrile:

- the hydrocyanation of butadiene - this process is currently not used in the UK;
- the ammonolysis of adipic acid - this is old technology and only recently ceased production in the UK; and
- the electrohydrodimerisation of acrylonitrile currently the most extensively used process worldwide and operated in the UK.

## Electrohydrodimerisation of acrylonitrile

In this process adiponitrile is produced by the electrohydrodimerisation of acrylonitrile. This is carried out in reactors that contain lead-plated carbon steel electrodes, which are periodically replaced as the product selectivity falls and the electrodes corrode.

A fall in the selectivity is indicated by a change in the off-gas concentration, a higher voltage drop across the electrodes and the presence of more reaction by-products. At this stage the electrolyte must be removed to storage and the reactor water washed. These wash waters contain lead and must be carefully monitored and reprocessed. The spent electrodes are processed for steel recovery.

The exit streams from the reactor consist of oxygen produced at the anode containing organics such as acrylonitrile, adiponitrile, propionitrile (formed by the hydrogenation of acrylonitrile), tricyanohexane (formed by the trimerisation of the acrylonitrile), and also hydrogen, iron and lead.

The reactor exit stream is routed via a two-stage separation system. The initial stage separates out the off-gases whilst the second stage is a gravity settler in which the electrolyte and organic phases are separated. The aqueous phase is fed to an extraction system and the organic phase is sent for adiponitrile recovery.

Off-gases from the separator pass to a scrubber, through which adiponitrile is recirculated, before discharge to atmosphere. This is important during start-up conditions when the system is saturated with acrylonitrile.

In the adiponitrile recovery section unreacted acrylonitrile is recovered and fed back to the extraction stage. This will also contain some of the electrolyte and any other additives. In addition the propionitrile can be recovered and either used as a raw material, sold or sent for disposal. It has a high calorific value and may be suitable as a support fuel for incineration. An adiponitrile stream is produced that requires further purification.

The adiponitrile is vacuum distilled to produce an adiponitrile product stream and high- and low-boiling fractions that include the trimers of acrylonitrile, which are suitable for incineration. Vacuum exhausts from each of the columns are scrubbed with chilled adiponitrile.

Recovered streams from the separator unit and the acrylonitrile recovery stage are fed into an extraction unit in which the adiponitrile and additives can be recovered and recycled to the reactor inlet. Iron, lead and electrolyte remain in the aqueous phase.

A crystalliser is used to reclaim the majority of the phosphate and borate species from the electrolyte.

The aqueous phase from the crystalliser is sent for lead removal in which sodiumhydrogen sulphate is added to form a lead

sludge, which can be separated by centrifuge. The aqueous waste stream after this operation must be carefully monitored for lead levels and further downstream treatment is required to reduce lead to acceptable levels. This, however, will produce a solid waste containing lead for disposal.

### (c) Hexamethylenediamine

Hexamethylenediamine (HMD) is currently produced by the catalytic hydrogenation of adiponitrile. Older processes based on the amination of hexanediol are no longer operated.

Two versions of the process are currently available as either a high-pressure process or a low-pressure process.

In the high-pressure process liquid ammonia is used to suppress the formation of by-products and, with typical hydrogenation temperatures of 80 to 150°C, this results in operating pressures in the range 200 to 340 barg to maintain the ammonia in the liquid phase.

In the low-pressure process alcohols and/or an aqueous alkali are used to suppress the formation of by-products and this results in a lower operating pressure.

The hydrogenation catalyst used for the reaction can take the form of either a catalyst slurry or a fixed bed. Patented catalysts used include reduced cobalt, iron, ruthenium or Raney nickel.

Impurities in the adiponitrile feedstock are hydrogenated and tend to form low-boiling impurities in the reactor system. Several by-products are also formed including hexamethyleneimine (HMI), bis-hexamethylenetriamine (HMT) and 1, 2-diaminocyclohexane (DACH). One by-product only formed in the low-pressure process is 2-aminomethylcyclopentylamine (AMC) produced by the caustic-catalysed rearrangement of adiponitrile.

#### *Low pressure process*

The basic raw materials for this process are adiponitrile, sodium hydroxide, hydrogen and the Raney nickel catalyst (stored under water).

Hydrogen is used in excess in the reaction, which is carried out at pressures around 35 barg and at temperatures below 100°C. The reactor is a gas-lift design.

The reaction mass consists of two liquid phases and a solid phase. The major liquid phase is the crude HMD product, whilst the solid phase is the Raney nickel catalyst. The minor liquid phase consists of concentrated caustic.

Crude product is decanted from the separation vessel and the clarified HMD product continuously separated from the solid phase and the concentrated caustic phase. Both these latter phases are returned to the reactor, whilst the product phase is fed through hydrocyclones to remove entrained catalyst before refining.

Catalyst is continuously removed from the reactor, washed and a

portion returned to the reactor along with fresh catalyst. The remainder can be sold into the metals recovery industry.

In the refining section the crude HMD is distilled to remove low- and high-boiling-point impurities and water.

A series of distillations generates a low-boiling fraction, pure HMD and a high-boiling HMD, which can be further batch-distilled under vacuum to recover HMD before disposal of the residues.

Water recovered in the refining stage contains some HMD and imines, which can be recycled to the reactor via the catalyst washing stage.

Both the high and low boilers have no commercial value and are usually incinerated, with energy recovery.

#### *High-pressure process*

The basic raw materials for this process are adiponitrile, liquid ammonia, hydrogen and an iron catalyst.

The ammonia is used in excess and over 80% of the ammonia is recycled.

A two-stage trickle bed reactor system is used for the reaction and contains the fixed-bed catalyst. The fully reduced iron catalyst, which is pyrophoric and has a limited service life, requires regeneration in a hydrogen atmosphere.

Reactor temperature control and the age of the catalyst are critical to the formation of by-products. If the temperature is too high, the formation of the hexamethyleneimine is favoured, whilst if the temperature is too low, the formation of aminocapronitrile is encouraged. As the catalyst ages the production rate of HMD falls.

The reactor product passes to a separator, which operates at 180°C and 250 barg. The liquid product is removed from the base of the unit and let down to 40 barg. The off-gases pass through a secondary cooler to a secondary product separator where again the liquid bottoms are removed and let down to 40 barg. The off-gases from both units are recycled to the first reactor.

The liquid phase is sent to a let-down vessel where the pressure is reduced and dissolved gases are released and separated.

These gases, mainly hydrogen and methane, pass through a condenser where ammonia is removed before being sent through an absorber to recover any remaining ammonia and then a water scrubber before being used as a fuel gas.

The liquid from the let-down vessel contains ammonia and this is boiled off in an ammonia reboiler/still, condensed and recycled. The crude HMD from the bottom of this still is cooled and stored in a nitrogen-blanketed storage vessel. Vent gases from this stage are routed to the ammonia recovery system.



In this storage facility, water is added to the crude HMD and forms an azeotrope with the hexamethyleneimine impurity to facilitate its later removal by distillation.

Vacuum distillation is used to reduce impurities in the HMD to the low levels required, typically less than 20 ppm. The water/imine azeotrope fraction is removed along with light and heavy fractions, both of which contain significant quantities of HMD and are therefore processed further in a batch still. The light and heavy fractions can both be re-used. The light fractions can be sold and the heavy fractions can be used in any upstream adiponitrile plant by recycling to the adiponitrile purification process.

Purified HMD is mixed with water to prevent solidification of the pure form, which occurs at temperatures below 45°C. Storage tanks are nitrogen-blanketed to prevent product oxidation and discoloration.

Air leaks into columns operating under vacuum cause the formation of impurities. To prevent this, carbon dioxide is routinely added at the top of distillation columns.

#### (d) Acrylamide

Acrylamide is manufactured by the reaction between acrylonitrile and water in the presence of a copper-based catalyst to produce an aqueous solution of the product. Unreacted acrylonitrile can be recycled within the process to give almost complete chemical conversion.

Manufacture of acrylamide involves continuous feeding of acrylonitrile and deaerated water into a continuous stirred tank reactor operating at 100°C and 4 barg, together with a catalyst stream.

The demineralised water feed can come from scrubbing plant, vacuum pumps and water-flushed seals. By this method any product or acrylonitrile losses are recycled to the reactor system and overall losses can be minimised.

The catalyst carry over in the reactor exit stream is removed by filtration before passing to a purification system. Acrylonitrile and product can then be reclaimed from this slurry by steam stripping and returned to the process, whilst the remaining effluent slurry consisting of water, filter precoat and copper catalyst are sent for disposal.

The purification system consists of a vacuum distillation column followed by a wiped film evaporator. Unreacted acrylonitrile and water are removed overhead and condensed by water-cooled and refrigerated condensers before being recycled back to the reactor. The product stream is a 50 wt% aqueous solution of acrylamide.

Off-gases from the condenser system, which pass to the vacuum system, will contain acrylonitrile and these are scrubbed to reclaim the acrylonitrile. The water used to irrigate these scrubbers can be used as the primary feed water to the reactor.

The 50 wt% aqueous solution of acrylamide can be further

purified by passing through an activated carbon adsorption column followed by an ion exchange column to remove cations (mainly copper). The spent carbon is disposed of periodically. Any copper passing through the screening filters renders the carbon unsuitable for regeneration.

The ion exchange columns are periodically regenerated with acid. This acid stream is neutralised with caustic soda solution to precipitate copper hydroxide, which can be filtered and disposed of. The filtrate, containing some acrylamide and copper, must also be sent for disposal.

#### (e) Pyridines and their derivatives

##### *Pyridine*

Pyridine is manufactured worldwide by the catalysed ammonolysis of acetaldehyde and formaldehyde but is presently not produced in the UK.

##### *Methylpyridine*

Methylpyridine is not produced in the UK in significant quantities but is a by-product of the 2,2'-bipyridyl manufacturing process, which involves the use of pyridine.

##### *Dimethyl pyridine*

Dimethylpyridine is not produced in the UK in significant quantities although a batch fraction can be produced as a by-product from a wet pyridine recovery plant.

## 2.4 Acids and aldehydes

### 2.4.1 Introduction

Production units for these chemicals range from large dedicated petrochemical-type facilities to small multi-purpose chemical plants that are run on a campaign basis. The major processes described here are all continuous. The characteristics of batch processes are described in IPCGN S2 4.02<sup>(6)</sup>.

### 2.4.2 Acetic acid

#### (a) General

Currently worldwide there are three main methods for the manufacture of acetic acid:

- acetaldehyde oxidation;
- liquid-phase catalytic oxidation of light hydrocarbons; and
- methanol carbonylation.

#### (b) Acetaldehyde oxidation

This process involves the catalytic air oxidation of acetaldehyde in the presence of manganese acetate at 50–80°C and 10 barg. The oxidation reaction product is distilled to remove gases including unreacted acetaldehyde, methyl acetate, acetone,

carbon monoxide, carbon dioxide and nitrogen. Crude glacial acetic acid is obtained, with impurities of formaldehyde and formic acid. Final purification of the acid involves distillation in the presence of potassium permanganate, sodium dichlorate or other oxidants.

This process is not currently used in the UK and is not described further.

### (c) Liquid-phase catalytic oxidation of light hydrocarbons

Acetic acid is manufactured by the liquid-phase catalytic oxidation in air of light hydrocarbons at a temperature between 150 - 200°C and a pressure between 40 and 50 barg. The aqueous reaction product is purified in a series of distillation columns producing acetic, formic and propionic acids and acetone. Lean off-gas from the reactor is dried and then recovered in activated carbon beds. Remaining gas is fed to a thermal destruction unit.

#### *Releases to air*

- The light hydrocarbon off-gas from the activated carbon beds/thermal destruction system.
- Acetic acid, acetaldehyde, acetone, carbon monoxide and other organics from vacuum pump discharges.
- Scrubbed vent gases from the acetone recovery unit containing acetone, methyl acetate, benzene, acetic acid, methyl ethyl ketone, esters, methanol and some high-boiling-point components.

Special control techniques: thermal oxidation of reactor off-gas, including recovery of heat and power by use of offgas expanders and waste heat recovery.

#### *Releases to water*

- Acetic acid, ketones, methanol, and acetaldehyde from vacuum systems.
- Final residues of butyric and succinic acids; aqueous streams from the distillation unit.
- Water from the acetone recovery unit containing methanol, ethanol, and traces of acetone and sodium salts.
- A discharge from the hydro-extractive distillation of propionic acid containing propionic acid, acetylacetone and 2,4-hexadiene.

#### *Releases to land*

- Waste from dryers, activated carbon beds and catalyst systems.
- Corrosion products containing a glass lead mixture contaminated with nickel oxalate and oxides of chromium and iron.

### (d) Methanol carbonylation

There are two distinct process variants for methanol carbonylation to acetic acid. The first process variant involves the use of a pressure of 700 barg, and Hastelloy C as the construction material. Copper and cobalt catalyst systems in the presence of iodine are also used. The other process variant is based on the use of rhodium/phosphine complexes as the catalyst system, together with hydrogen/methyl iodide as promoter. Operating pressures of 33-36 barg and temperatures of 150-200°C are utilised. Purification involves multiple distillation to remove the catalyst mixture, water, mixed acids and other impurities.

#### *Releases to air*

- High-pressure off-gas from the reactor, which is absorbed and scrubbed in a light ends recovery system before venting to a thermal destruction unit and contains small quantities of hydrogen iodide.
- Flared light ends from the first two distillation columns which pass via a low-pressure absorber system containing chilled acetic acid before being vented to a thermal destruction unit, again containing small quantities of hydrogen iodide.

Special control techniques: off-gas scrubbers, using methanol or acid recycled back to the process.

#### *Releases to water*

- Liquor from iodine scrubber during catalyst addition.
- Liquor from the final column light ends scrubbers contaminated with acetic acid.

#### *Releases to land*

- Heavy fractions from the heavy acids column, comprising propionic and acetic acids together with potassium salts and catalyst.

### 2.4.3 Acetylene

There are a number of processes for the manufacture of acetylene. These include:

- from hydrocarbons  
pyrolysis,  
natural gas oxidation,  
electric arc;
- from calcium carbide  
Dry Hydrolysis,  
Wet hydrolysis.

Acetylene is used in the UK primarily as a fuel gas and not as a chemical intermediate. It requires a production process that can

be stopped and started according to market demand.

In the UK, all acetylene is produced by the chemical reaction between calcium carbide and excess water in a generator. The manufacturing process can be subdivided into the following stages:

- calcium carbide handling;
- gas generation;
- purification;
- collection and processing of lime; and
- charging of cylinders.

Calcium carbide is fed into the generator and water added for both reaction and cooling purposes.

A by-product of the reaction is calcium hydroxide (lime), which is removed from the generator to settling tanks or pits. The acetylene leaving the generator is contaminated with the hydrides of the impurities that were present in the carbide.

After ammonia scrubbing and removal of hydrogen sulphide and phosphine, the acetylene is passed through a dryer. Calcium chloride or molecular sieve may be used as a drying medium. Currently, calcium chloride is used in the UK. After purification and drying, the acetylene is compressed and charged into cylinders under pressure, where it is dissolved into acetone contained in a porous medium (mass). Typically acetone storage tanks are blanketed with nitrogen.

#### *Releases to air*

- Acetylene, ammonia, hydrogen sulphide and phosphine from purging of the generator feed hopper;
- Acetylene from the purification bed vent during regeneration.
- Ammonia and hydrogen sulphide from lime pits.

#### *Releases to water*

- Glycol from raw gas holding tank condensates (contributing to BOD (biological oxygen demand) and COD (chemical oxygen demand) waste water loadings).
- Arising from acetylene cooling and water vapour condensing out and combining with the gas holder glycol water seal.
- Oil from compressors.
- Calcium chloride from dryer blow-down.
- Ammonia and hydrogen sulphide from the ammonia scrubber used to purify raw acetylene.

#### *Releases to land*

- Carbon and ferrosilicates from the generator (the result of unreacted impurities in the carbide)

- Chromium and mercury from spent purifier bed solids.

### **2.4.4 Acetic anhydride**

#### **(a) General**

There are two main methods for the manufacture of acetic anhydride:

- acetic acid/ketene route (positive- or reduced-pressure cracking); and
- carbonylation of methyl acetate.

The acetone/ketene route is not currently used in the UK.

#### **(b) Acetic acid/ketene route (positive or reduced pressure cracking)**

The first stage is the catalytic endothermic decomposition of acetic acid to give ketene and water. A temperature of 700°C and reduced pressure are used. Alternatively positive pressure may be used. Product vapours from the process comprise ketene, some unreacted acetic acid and by-products.

The second stage involves the addition of ketene to acetic acid under reduced pressure to give acetic anhydride. Acetic anhydride is recovered by distillation.

#### **(c) Carbonylation of methanol**

This process involves the esterification of methanol with acetic acid (possibly from a recycle source) or a portion of the product acetic anhydride, to produce methyl acetate. Carbonylation of methyl acetate yields acetic anhydride. This route is associated with the carbonylation of methanol to acetic acid (see Section 2.4.2).

### **2.4.5 Adipic acid**

The commercial manufacture of adipic acid is achieved in two stages. The first stage is either the oxidation of cyclohexane or the hydrogenation of phenol to give a cyclohexanone/cyclohexanol mixture (known as KA or ketone alcohol), which is purified by distillation. The catalyst is recycled via a crystallisation system. In the second stage KA is oxidised with nitric acid. The catalyst is a copper salt. The process releases substantial quantities of nitrous oxide ( $\text{N}_2\text{O}$ ), which has a high global warming potential. Its release should be minimised by thermal reduction in the presence of methane or by catalytic reduction. Purification of adipic acid involves crystallisation and centrifuging.

A simplified process flow diagram is shown in Figure 2.6.

#### *Releases to air*

- Oxides of nitrogen and nitrous oxide from the stripping columns and crystallisers.

- Adipic acid particulate from drying and handling.
- Other organics from feedstock and absorbers and purification columns on the KA section.
- Caproic, adipic, valeric, butyric, propionic and acetic acids (all of which have pungent odours) from acid handling and storage.

Special control techniques: of relevance to adipic acid production focus on the abatement of the stream containing nitrous oxide. Techniques used internationally include catalytic treatment and thermal destruction in reducing conditions.

#### Releases to water

- KA catalyst and organics from KA purification.
- Oily water.
- Low- pH waste streams containing adipic, boric, glutaric and succinic acids with copper, vanadium and sulphuric acid.

Special control techniques: ion exchange systems to remove inorganic salts, such as copper or vanadium salts from catalysts; evaporation and crystallisation to recover boric acid and other by-products.

#### Releases to land

- KA catalyst from plant cleaning.
- Non-volatile organic residues and organic recovery tails from KA production.
- Wastes on shut-down, ie tar-contaminated sand, oxidiser residues, KA sump dredgings.
- Boric acid sweepings.
- Caustic wash residues.

#### 2.4.6 Formaldehyde

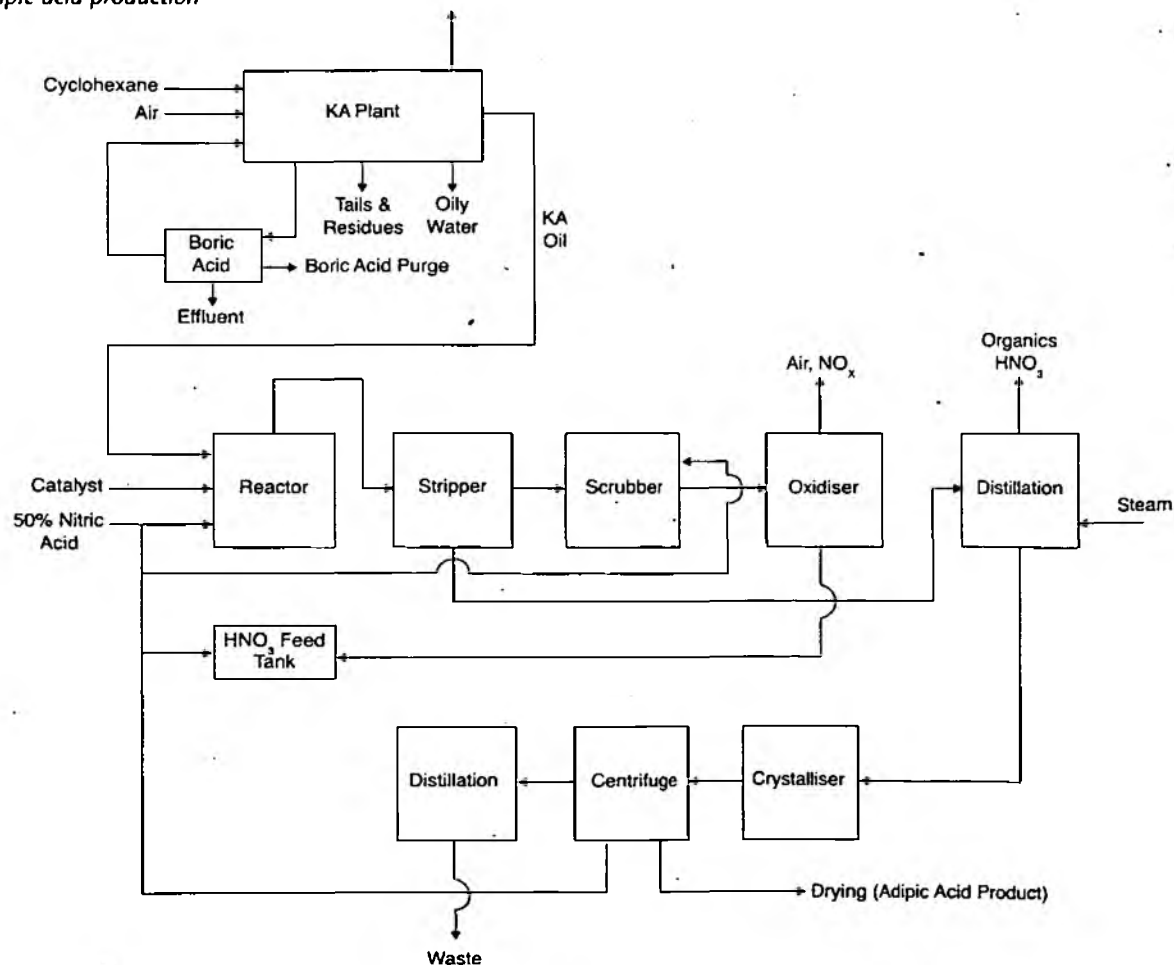
Formaldehyde is manufactured by three main processes:

- silver catalytic oxidation;
- metal oxide catalytic oxidation; and
- combi process.

##### (a) Silver catalytic oxidation

In the silver catalytic oxidation route methanol is reacted with oxygen over a silver catalyst, at atmospheric pressure and a temperature of 600-650°C. Side-reactions are minimised by cooling rapidly to 500°C.

Figure 2.6 Adipic acid production



**(b) Metal oxide catalytic oxidation**

In the metal oxide route the same raw materials are used as in (a), but the catalyst is an iron molybdenum oxide compound. Performance enhancement is achieved by adding small amounts of other metal oxides, for example chromium oxide. The reaction takes place at atmospheric pressure and at temperatures of 300-400°C. The metal oxide process accounts for the majority of recent construction internationally. A simplified flowsheet is shown in Figure 2.7.

**(c) Combi process**

In the Combi process route there is a combination of silver and metal oxide reactions. This combination can eliminate the need to recover and recycle methanol in the silver catalyst process by using a two-stage oxidation system. Methanol is partly converted using a silver catalyst, the products are cooled, then excess air is added to convert the remaining methanol over a metal oxide catalyst.

In all cases the formaldehyde is produced in the form of an aqueous solution by absorbing the reactor gas in water. The methanol content can be reduced by distillation, the methanol being returned to the reactor.

**Releases to air**

- Absorber tail gas with formaldehyde and related organics; this is usually destroyed by thermal (silver process) or catalytic incineration.
- Fugitive emissions for equipment and fittings; high-integrity pumps and minimal flanges are used on some plants internationally.
- Evaporative losses of formaldehyde and methanol from tanks and transfer; wet scrubbing can be used.

**Releases to water**

- Contaminated condensate and wash water.

**Releases to land**

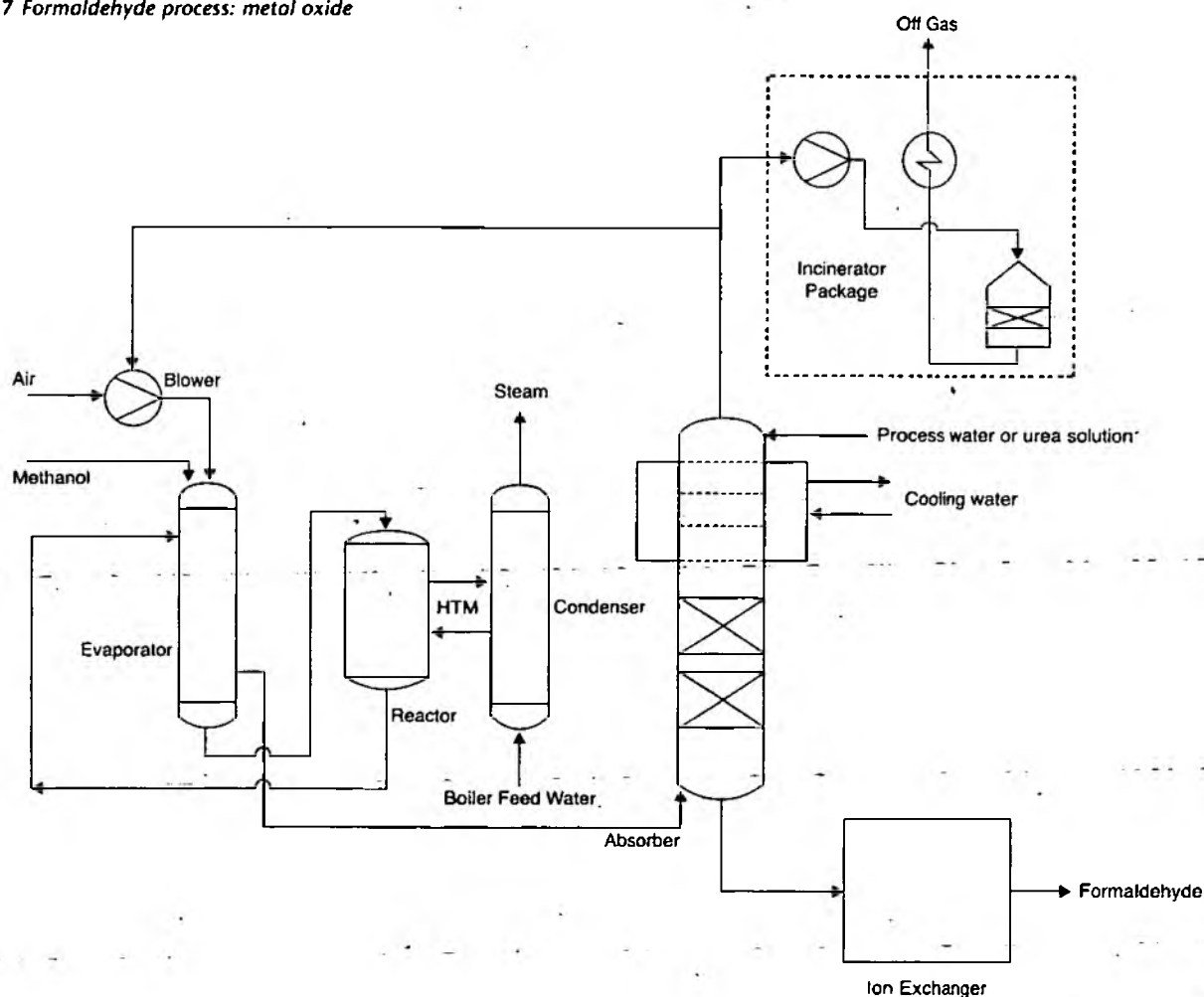
- Spent catalyst.

**2.4.7 Formic acid**

Four methods are used to produce formic acid:

- by-product of acetic acid manufacture;

Figure 2.7 Formaldehyde process: metal oxide



- methyl formate route;
- methyl formate via formamide route; and
- sodium formate route.

In the UK, large-scale manufacture of formic acid is as a by-product of acetic acid manufacture by liquid-phase catalytic oxidation. Refer to Section 2.4.2 above.

#### 2.4.8 Methacrylic acid

There are two main routes for the manufacture of methacrylic acid (MAA):

- acetone cyanohydrin process; and
- vapour-phase catalytic oxidation from isobutylene or tertiary butanol.

Of these only the acetone cyanohydrin process is employed in the UK.

The acetone cyanohydrin process comprises five process stages (Figure 2.8). The first, conversion of the cyanohydrin to an amide, is undertaken in a stirred reaction vessel. From there the reactants pass to a hydrolyser where the amide is hydrolysed to methacrylic acid which is then recovered in a phase separator. The methacrylic acid passes forward for purification by distillation and the remainder by-product acid is distilled. Organic material is recovered for recycle and spent acid can be recovered via an acid recovery plant if available.

##### Releases to air

- Vent gases from the by-product acid separator.

- Vent gases from the reactor and hydrolyser containing carbon monoxide, sulphur dioxide, and organic compounds, including methacrylic acid.

In one control technique, fuel-rich vent can be sent to a vent gas burner, for destruction to  $\text{CO}_2$ ,  $\text{NO}_x$  and  $\text{N}_2$

##### Releases to water

- Waste streams from vacuum systems containing organics.
- Waste water from the organics recovery unit.

Special control techniques: recovery of organics from purge water.

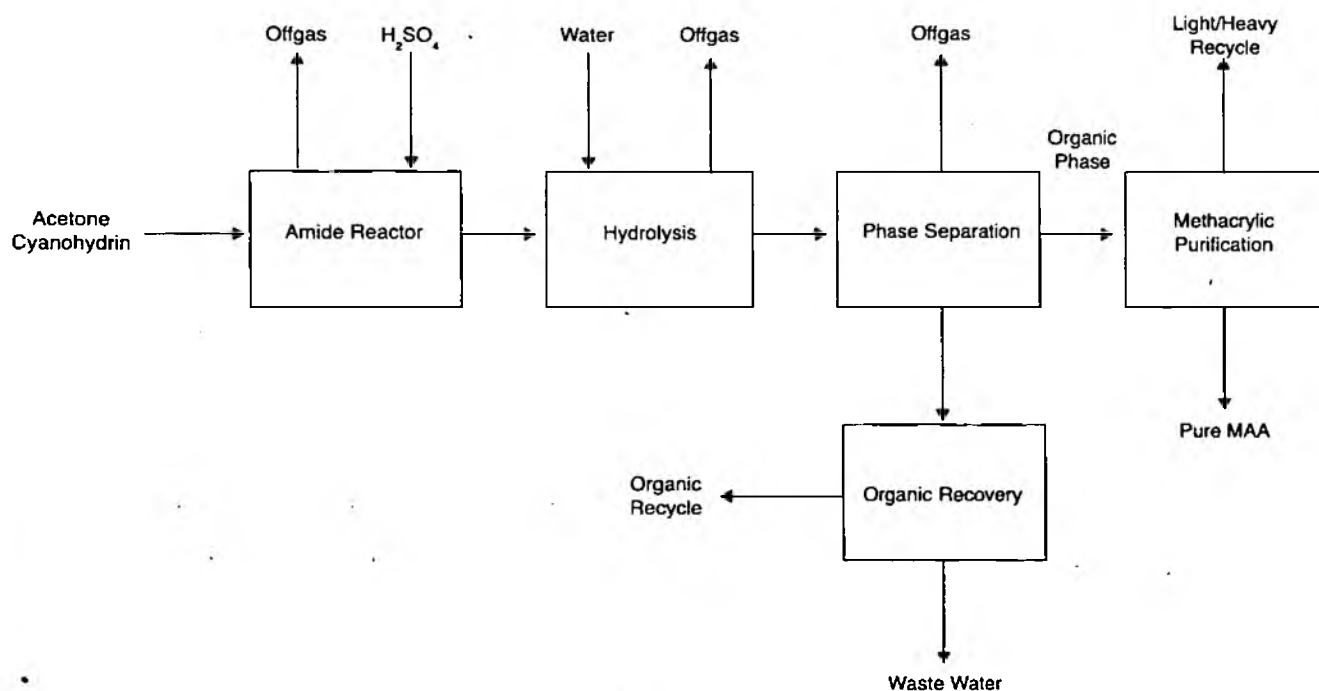
#### 2.4.9 Phthalic anhydride

Phthalic anhydride is manufactured by fixed-bed oxidation. In this process ortho-xylene or naphthalene and air are preheated and passed through the catalyst chamber. The reactor gases are subsequently cooled and passed through switch condensers where the crude product de-sublimes. The off-gases are either scrubbed or incinerated before discharge to the atmosphere. Crude product is distilled under vacuum to achieve the required purity. The following discharges relate to the ortho-xylene route.

##### Releases to air

- Off-gas from the switch condenser scrubber, containing phthalic anhydride, maleic anhydride, various acids, sulphur dioxide and carbon monoxide.
- Combustion products from incinerated residues and overheads from the distillation columns.

Figure 2.8 Manufacture of methacrylic acid





*Releases to water*

- Acidic scrubber liquor from the switch condenser off-gas scrubber or waste water from maleic anhydride recovery.

*Releases to land*

- Solid organic residues from distillation columns and stills.

Special control techniques: wet scrubbing of switch condenser off-gases, with recovery of maleic anhydride by processes such as azeotropic dehydration; catalytic incineration of scrubber tail gas, or condenser off-gas if no scrubber is installed; incineration or fuel use of all hydrocarbon residues.

**2.4.10 Propionic acid**

There are two main methods for the manufacture of propionic acid:

- by-product of acetic acid manufacture; and
- the OXO process.

Current UK production is via acetic acid manufacture. Refer to Section 2.4.2 for further details.

**2.4.11 Terephthalic acid**

Terephthalic acid is manufactured in a two-step process: First para-xylene is oxidised in acetic acid to produce a crude terephthalic acid (Figure 2.9). This is followed by selective catalytic hydrogenation of the crude product, to allow a purified terephthalic acid to be recovered (Figure 2.10). Both the oxidation and the purification steps employ crystallisation of the reaction products, followed by solid/liquid separation (by centrifuge or filter) and drying of solids to recover pure terephthalic acid (PTA) from the process solvents and other more soluble organic acids and aldehyde by-products.

*Releases to air*

- Off-gases from the oxidation stage containing carbon monoxide, acetic acid, methyl acetate, para-xylene and methyl bromide.
- Vent gases from solvent recovery column containing carbon monoxide, methyl acetate, para-xylene and acetic acid.
- Vent gases from the atmospheric absorber containing acetic acid and methyl acetate.
- Vent gases from purification plant scrubber containing terephthalic and acetic acids.
- Vent gases generated from the off-gas dryers containing methyl acetate, acetic acid and para-xylene.

*Releases to water*

- Aqueous condensate from solvent recovery and acetic acid dehydration columns containing acetic acid, formaldehyde, methyl acetate, para-xylene and methanol.
- Waste water from crude terephthalic acid purification stage containing para-toluic, terephthalic, benzoic and other organic acids, together with manganese and cobalt salts.
- Aqueous condensate from the residue treatment crystalliser steam ejectors.
- Washings from rotary vacuum filters, centrifuges and other process equipment.

*Releases to land*

- Filter cake from residue recovery area.

Figure 2.9 Terephthalic acid process: oxidation

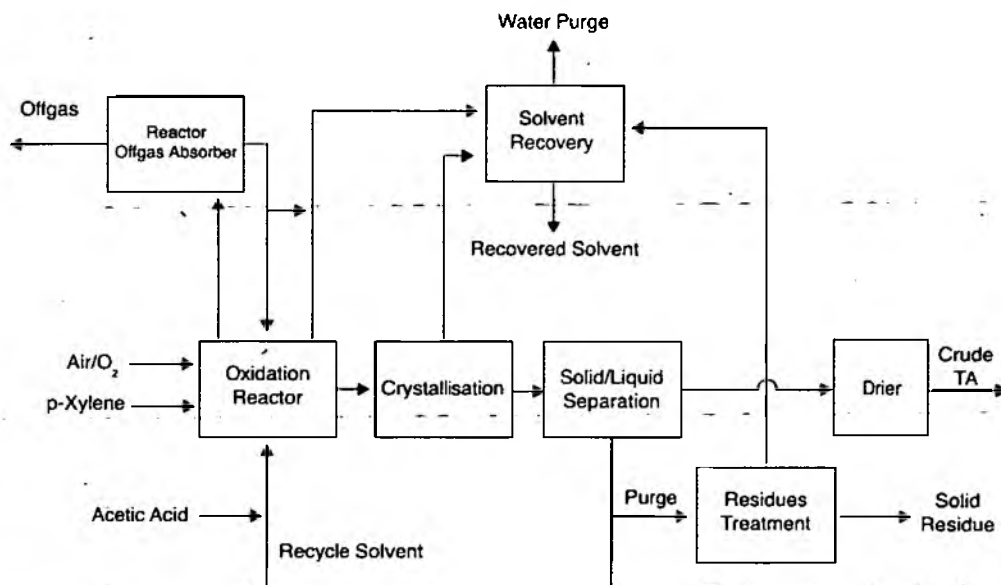
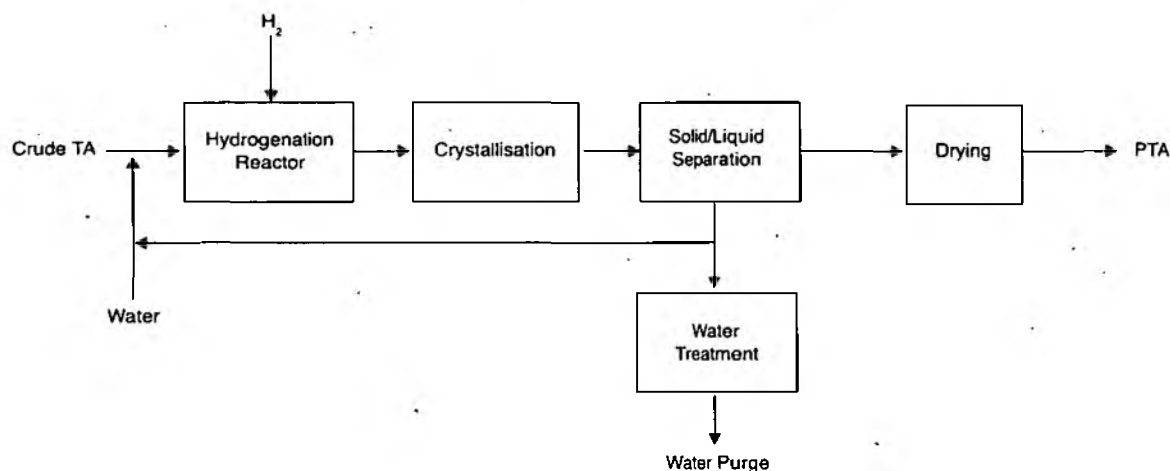


Figure 2.10 Terephthalic acid process: purification



Special control techniques: solids including by-product organic acid and traces of catalyst are recovered as a solid residue; optimisation of the reactor conditions to minimise by-product production; lagoons to cope with high BOD loads resulting from washings of equipment, or operational problems caused by process blockages.

## 2.5 Sulphur compounds

### 2.5.1 Introduction

Reference should be made to Section 3 for more general considerations relating to the prevention of discharges and for the abatement of pollution from manufacturing plant and from the use of the compounds covered by this section.

There are several pollution control considerations common to all processes involving sulphur-containing organic chemicals: these are presented collectively in Section 2.5.8.

The low odour thresholds of many sulphur compounds have resulted in the wide use of technologies designed to minimise releases such as all-welded pipework, canned pumps, scrubbing equipment, etc., in preference to the use of conventional designs (flanged pipework, centrifugal pumps, non-scrubbed vents, etc.), which are more prone to fugitive and continuous releases.

### 2.5.2 Carbon disulphide-hydrocarbon-sulphur process

Carbon disulphide is manufactured by the reaction of sulphur and hydrocarbons such as methane, ethane, propylene or natural gas. The gas is usually preheated and then mixed with vaporised sulphur. The mixture is then heated to between 580–650°C and pressures between 2.5 and 5 barg to produce carbon disulphide and hydrogen sulphide. Uncondensed carbon disulphide is recovered from the hydrogen sulphide by absorption in odourless kerosene, followed by steam stripping, and the combined carbon disulphide streams are purified by distillation. The hydrogen sulphide is converted back to sulphur in a Claus plant.

#### Releases to air

- The furnace flues contain standard combustion products from natural gas. A white plume and brown cloud can be generated if there is a furnace tube failure.
- ⊗ Carbon disulphide and hydrogen sulphide, stripped by steam from the stabiliser feed drum overflow, are sent to the flare system.
- ⊗ The gases leaving the absorber column contain hydrogen sulphide, sulphur and carbon disulphide. After passing through a wire-mesh filter to remove entrained droplets, the gases are passed to a Claus unit to recover sulphur.
- ⊗ The carbon disulphide surge tank vent is kept live with a methane (natural gas) blanket leading to a continuous discharge to the flare system. This may be contaminated with carbon disulphide.
- Compressed air is used to strip out carbon disulphide from the surge tank catch pot overflow. This may form a stream containing a significant concentration of carbon disulphide, which requires treatment.
- Odourless kerosene from the production plant may be used to absorb carbon disulphide vapours emitted during the filling of tankers.
- ⊗ Jacketed pipework from sulphur condensers discharge to flare stack. During furnace start-up, a methane feed is established, and sulphur slowly brought on-line until the desired conversion is achieved.

#### Releases to water

- ⊗ The aqueous layer from the stabiliser feed drum is degassed with steam and passed to a catch pot to which cold water is added.
- A purge of the lean oil system is completed to prevent the build-up of sulphur compounds. This is stripped using a polysulphide caustic liquor.

- Following aeration with compressed air, the surge tank catch pot overflow discharges to the site effluent drains.
- Spillage into the tanker loading sump is not normal and therefore water displaced by rainfall is generally the only discharge from this source.

#### *Releases to land*

- The sulphur filters are coated with diatomaceous earth. This, together with some sulphur and inorganic impurities, is removed at intervals.

### 2.5.3 Dithiocarbamates

An aqueous alkaline solution of secondary or tertiary amines is reacted with carbon disulphide to form aqueous dithiocarbamates.

Aqueous dithiocarbamates can be added to an aqueous metal salt to produce a slurry of the metal dithiocarbamate. The dithiocarbamate is then filtered and dried. Zinc, nickel and copper dithiocarbamates are the main products.

### 2.5.4 Thiols

Some of the preferred methods for manufacturing thiols are outlined below.

Ethanethiol is prepared by the vapour-phase reaction between ethylene and hydrogen sulphide over an acid catalyst. Methanethiol is similarly prepared from the corresponding alcohol.

Other primary thiols are prepared by the UV-light-promoted addition of hydrogen sulphide to primary alkenes. This reaction occurs in the liquid phase, with a free-radical mechanism. Medium-pressure mercury lamps, or other free-radical generators such as azonitriles, are used as promoters. Excess hydrogen sulphide is used to minimise the formation of by-products such as the addition product of thiol and alkene.

Tertiary alkanethiols are prepared from the corresponding tertiary alkene and hydrogen sulphide, in a continuous flow reaction over a solid catalyst. For example, 2-methyl-2-propanethiol is made from isobutylene. Catalysts used include aluminium chloride, other acid halides, hydrogen fluoride and boron trifluoride.

Thiophenol is prepared by the red phosphorus reaction of benzenesulphonyl chloride. Another route is the high-temperature reaction of monochlorobenzene and hydrogen sulphide.

Thiols are transported as liquids – they are flammable and volatile. Process equipment and storage vessels should be constructed of carbon steel, aluminium, stainless steel or other copper-free alloy. Thiols stored in carbon steel should be kept dry and blanketed with an inert gas to prevent the formation of iron sulphur complexes. Rubber is not suitable for hoses or gaskets.

#### *Releases into air*

- As a result of opening drums for transfer of contents to reactors, vapours are emitted that are usually locally extracted. These are usually passed either to carbon adsorbers or, if available, to a lean gas main and incinerated.
- Used drums are sent to a drum decontamination plant where they are slightly heated. The extracted vapours are adsorbed or, if appropriate, collected in a lean gas main for incineration or alternatively caustic scrubbed.
- Blending tanks are vented either to a carbon adsorber or, if appropriate, to a lean gas line for incineration or caustic scrubbed.
- Road tankers are equipped with a carbon adsorber to remove residual odours.
- Spent tanker wash-down methanol is usually incinerated.

#### *Releases to water*

- The final water flushing of tankers containing unspent hypochlorite is discharged to effluent treatment.

#### *Releases to land*

- Spent caustic solution from back-up incinerator scrubbers is usually landfilled.
- Sludges and filter cakes from effluent treatment containing dithiocarbamates and other sulphur complexes are sent to landfill.

### 2.5.5 Thiophene

There are three commercial processes for the production of thiophene.

#### (a) Furan and hydrogen sulphide

The vapour-phase reaction between furan and hydrogen sulphide over a heteropolyacid-promoted metal oxide catalyst at 300-400°C gives thiophene and water as reaction products. These are separated and crude thiophene is continuously distilled to produce a high-purity product. The catalyst has a long service life and does not need periodic regeneration. The same process can be used to manufacture 2-methylthiophene from 2-methylfuran, and tetrahydrothiophene from tetrahydrofuran.

#### (b) C<sub>4</sub> compounds and carbon disulphide

C<sub>4</sub> raw materials (1-butene, butadiene, n-butanol and 2-butenal) undergo continuous reaction with carbon disulphide over an alkali-promoted metal oxide catalyst at 500°C. Yields vary according to the starting material. The catalyst must be periodically regenerated to remove surface coke build-up. The process may be used for the manufacture of 2- and 3-alkylthiophenes.

**(c) Butane and sulphur**

This process involves the continuous reaction of butane and sulphur at 500–600°C over a mixed metal oxide catalyst. The hydrogen formed reacts exothermically with the sulphur feed to give hydrogen sulphide. Hydrogen sulphide then reacts with butane residue to yield thiophene. Periodic air regeneration of the catalyst is required. The process may also be applied to the production of 2- and 3-alkylthiophenes from higher hydrocarbons.

**2.5.6 Ethyl pentachlorothiophene**

Phosphorus pentasulphide and ethanol are reacted together to form diethyldithiophosphoric acid (DETA). Hydrogen sulphide is liberated in this process. If the reactor temperature were allowed to rise to 150°C, ethyl thiol would be generated. Ethanol is used to scrub the reactor vent gases before entering the reactor. Ethyl pentachlorothiophene (EPCT) is produced by chlorination of DETA when sulphur is precipitated. The hydrogen chloride liberated is absorbed and residual gases passed through a caustic scrubber to an incinerator. EPCT is distilled off into a second receiver leaving the heavier residues in the distillation still. Prolonged distillation can lead to additional thiols being generated.

***Releases to air***

- Breathing releases from the ethanol storage tank are released directly to the atmosphere.
- Off-gases from the reactor are incinerated with contaminated combustion air drawn from the building caustic scrubber discharge and storage tank vents.

***Releases to water***

- Spent scrubber liquor is discharged frequently.
- 32% hydrochloric acid is generated in the adsorber (water scrubber) from hydrogen chloride fumes. This is usually sold commercially or can be used to neutralise alkaline liquid waste streams from elsewhere on site.

***Releases to land***

- Cartridges from the DETA filter are collected and sent for off-site disposal.
- The residues generated in the chlorination are discharged to steel drums loaded on a conveyor. Operators are protected by screens through which the building ventilation air is drawn into the tunnel and to the incinerator. Drums are allowed to cool before lidding and are sent to landfill.

**2.5.7 Mercaptobenzothiazole**

Mercaptobenzothiazole (MBT) is produced by the reaction between aniline, carbon disulphide and sulphur, and produces hydrogen sulphide as the main by-product. Other by-products

include benzothiazole (BTH), anilinobenzothiazoles, aminophenols and thiocarbanilides.

MBT is a solid product handled in the form of dry preformed pellets, which are generally non-dusty.

MBT is produced in a batch reaction. Sulphur is charged from hot molten bulk storage and carbon disulphide and aniline from bulk storage. The reaction is carried out at over 200°C and greater than 50 barg. The hydrogen sulphide produced must be released from the reactor system under pressure control. After completion of the reaction, the molten MBT is dissolved in sodium hydroxide and extracted with toluene which is recovered for re-use. BTH and aniline are recycled to the reactor after separation by distillation from tarry residues which are drummed for disposal. An alternative route uses steam distillation.

**2.5.8 Releases to the environment (general considerations for sulphur compounds)**

The following sections are relevant to most processes involving organic chemicals containing sulphur.

***Releases to air***

- Waste process gases are likely to contain hydrogen sulphide and should, where practicable, undergo sulphur recovery. A typical sulphur recovery unit is described in Section 2.5.9.
- During normal operation, waste streams containing mainly carbon disulphide are adsorbed in odourless kerosene. The resulting stream containing hydrogen sulphide, sulphur and carbon disulphide could be incinerated to give sulphur dioxide as well as carbon oxides and water vapour. Methods to minimise the release of sulphur oxides should be considered. Where appropriate sulphur recovery units should be installed upstream of any incineration equipment.
- Contaminated extraction air can be dealt with most easily by incineration. Otherwise, carbon or biological filters may be considered. Amine, caustic scrubbing or other systems may be appropriate for particular releases.

- Odour problems are particularly prominent in the manufacture of thiols and other organic sulphur compounds. Adsorption beds and biofilters may be used to eliminate odours from fugitive releases in enclosed areas.

***Releases to water***

- Liquid effluents will originate from scrubbing systems, process wastes and routine cleaning of equipment. The effluents may contain carbon disulphide, or hydrogen sulphide, mercaptans or other organic sulphur compounds.

- Effluents are likely to require primary and secondary treatment prior to discharge to the environment.
- Aqueous wastes contaminated with kerosene (carbon disulphide process) will require oil separation. Where possible, contaminated kerosene should be regenerated on-site by stripping with a polysulphide caustic liquor.
- Spent scrubber liquors can be treated with hypochlorite to form inert chlorates of sulphur. The use of hypochlorite or other easily handled oxidant (such as hydrogen peroxide or ozone) should be considered for the elimination of odours in effluent.

#### *Releases to land*

- Wastes intended for disposal to land are likely to contain organic sulphur compounds. Operators should ensure that these compounds are removed prior to the landfill of wastes or that the wastes are suitably contained to prevent the release of the sulphur component.
- Releases to land may include spent consumables from the process such as drums, sacks and rags. These may be contaminated with sulphur compounds and therefore generate odours.

### 2.5.9 Sulphur recovery

There are several recovery techniques currently employed utilising scrubbing-type processes. Examples include the following.

#### **(a) Mono- and diethanolamine processes**

The amine compounds react with hydrogen sulphide and carbon dioxide to form inert compounds.

The amine absorbent passes counter-currently to the sour gas in a packed column: sweetened gas passes for further treatment. The rich amine stream is transferred to a feed drum, which also separates entrained hydrocarbons.

Methyldiethanolamine (MDEA) features in many of the most modern amine blends. They have a good absorption efficiency and can be tailored to suit particular waste streams.

#### **(b) Hot carbonate processes**

This process utilises the same operations as the MDEA process above except that the absorbent is potassium carbonate.

#### **(c) Sulfinol process**

In order to avoid the degradation losses suffered by MDEA solutions, some plants have switched to the solvent sulfinol. The sulfinol solution usually consists of 40-45 wt% sulfolane (tetrahydrothiophene dioxide), 40-45% diisopropanolamine, and the balance water. Sulfinol provides greater gas-treatment capacity, lower solvent circulation, lower heat requirements, and lower rates of solvent degradation.

#### **(d) Alkazid process**

The alkazid process is a cyclic heat regenerative type. It uses a solution containing the potassium salt of N,N-diethylglycine or N,N-dimethylglycine. This selectively absorbs hydrogen sulphide, carbon dioxide, small amounts of carbon disulphide, and hydrogen cyanide. The M solution, containing sodium alanine, absorbs hydrogen sulphide and carbon dioxide simultaneously. The S solution, containing sodium phenolate, absorbs carbon disulphide and mercaptans more effectively.

#### **(e) Claus sulphur recovery**

The rich amine stream from the scrubber passes to a regenerator column where heat is applied to drive off the hydrogen sulphide. The overheads are cooled, with condensate being recycled to the column, and the acid gas (greater than 90% hydrogen sulphide) is passed to the sulphur recovery unit and the lean amine stream is recycled to the scrubber.

A Claus sulphur recovery unit operating with "split" flow and three catalytic stages will be described. Part of the acid gas is burnt with air in a furnace to produce sulphur dioxide and water vapour. Further hydrogen sulphide then reacts with the sulphur dioxide to produce water vapour and elemental sulphur.

Both reactions occur in the combustion stage and sulphur is condensed and removed from the exit gases. Further acid gas is added in a reheater and the mixture is passed to the first catalytic stage, containing a fixed bed of bauxite, where the second reaction continues. The reaction is equilibrium-limited and overall conversion of hydrogen sulphide to sulphur depends upon the number of reacting and condensing stages. To achieve acceptable conversion, three stages are required, or two stages and tail gas clean-up.

Residual sulphur dioxide and hydrogen sulphide are passed to tail gas incineration before discharge to a vent.

Sulphur recovery plants should operate to a recovery efficiency of at least 98% during normal operation, which will normally require three catalytic conversion stages with the final stage utilising a selective catalyst (eg super-Claus process) or with further treatment of the tail gas (where residual sulphur dioxide is reduced to hydrogen sulphide, which can be recycled to the amine scrubbers). Notwithstanding this requirement, operators should demonstrate to the Inspector that they have, where appropriate, considered further abatement techniques to achieve the benchmark release level. New plant should use enhanced sulphur recovery techniques.

Sulphur recovery units operate efficiently over a limited throughput range and operators should take this into account when designing their facilities. Further details on Claus plants are given in IPCGN S2 1.10<sup>(11)</sup>.

## (f) Liquid redox processes

A viable alternative to amine stripping followed by sulphur recovery in a Claus unit is direct sulphur recovery from weak hydrogen sulphide streams by liquid redox.

Liquid redox technologies oxidise hydrogen sulphide in a liquid solution by the action of a number of mild oxidising agents to produce sulphur and water.

The Stretford process removes  $H_2S$  from effluent gases. It is a continuous liquid purification system that converts  $H_2S$  to elemental sulphur. The gas stream is first washed in an alkaline solution containing dissolved vanadates and anthraquinone disulphonic acids, fixing the hydrogen sulphide. The liquid from the washing stage then passes to a reaction tank, where virtually all the hydrogen sulphide is converted into elemental sulphur. The next stage, oxidation, separates the sulphur from the solution, which can then be returned to the washing stage. The sulphur is floated off as a froth for the final stage of recovery, when it can be recovered in a pure saleable form. The sulphur is usually recovered from the slurry in a molten form by decantation under pressure frequently with prior filtration and is obtained in a pure saleable form.

The vanadium-based Stretford process can achieve removal efficiencies of 99.9%. The process is tolerant to fluctuating flowrates.

However, the use of vanadium may have undesirable environmental implications. Other processes utilising non-toxic iron-based catalysts have been developed.

## 2.6 Monomers and polymers

### 2.6.1 Introduction

Most monomers are produced by continuous processes and their polymerisation may be either continuous or batch. Although the examples of polymerisation described below

refer mainly to single monomers, many copolymers are produced using two or more different monomers.

EC Directive 90/415/EEC<sup>(15)</sup> covers the manufacture and use of 1,2-dichloroethane (DCE) and is relevant to releases to water from the production of vinyl chloride monomer (VCM).

The Oslo and Paris Commission (OSPARCOM) has issued draft Recommendations on BAT for the manufacture of VCM (96/2)<sup>(16)</sup> and suspension poly(vinyl chloride) (PVC) (96/3)<sup>(17)</sup>. A Recommendation on BAT for emulsion PVC is being developed.

Inspectors should check the requirements of the Directive and the status of the Recommendations in their regulation of such processes.

### 2.6.2 Manufacture and storage of vinyl chloride

#### (a) Vinyl chloride manufacture

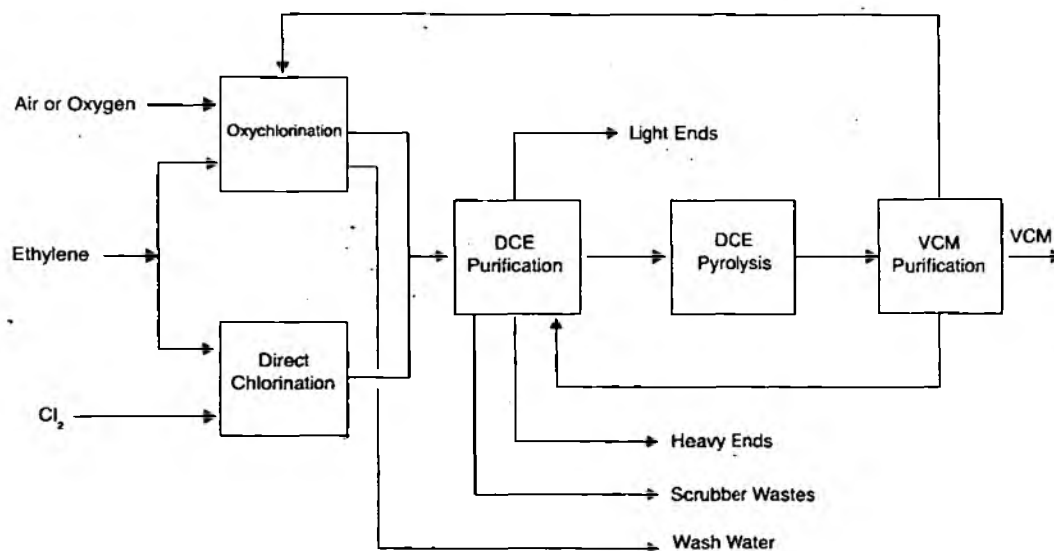
VCM can be manufactured commercially by two processes:

- hydrochlorination of acetylene in the presence of a mercuric chloride catalyst, which is now not usually economic; and
- cracking of 1,2-dichloroethane (DCE) to VCM and HCl.

The 'balanced process' shown in Figure 2.11 includes the formation of the intermediate DCE from ethylene and chlorine by direct chlorination and oxychlorination of ethylene with recycle HCl, followed by thermal cracking to form VCM.

Within the industry, 1,2-dichloroethane (DCE) is usually termed ethylene dichloride (EDC). The term DCE is used in this description. DCE is manufactured by the direct chlorination of ethylene, generally in the liquid phase. The reaction is catalysed by metal chlorides, including ferric, aluminium, copper and antimony chlorides, and substitution reactions are inhibited by oxygen.

Figure 2.11 *Balanced DCE/VCM production*



The process can be operated at high or low temperatures. The latter produces less by-products and allows the use of lower-grade construction materials, whilst the former produces DCE in the gaseous form and so the catalyst does not have to be removed by washing. The low-temperature (less than 100°C) route is the commonest in Europe.

Hydrogen chloride generated in the cracking of DCE to VCM is reacted in the gas phase in either a fixed-bed or fluidised-bed oxychlorination reactor containing a copper chloride catalyst with ethylene and either oxygen or air to produce DCE again. In the latter case, air and ethylene are fed in slight excess of stoichiometric requirements to ensure high conversion of hydrogen chloride; however, significant quantities of chlorinated by-products are formed. Use of oxygen in place of air requires a larger excess of ethylene in the feed, permits lower-temperature operation, and gives improved product yield with significantly reduced by-products and volume of vented gases. The reaction temperature is up to 350°C and at a pressure up to 130 barg.

DCE must be purified before cracking. The first purification stage consists of scrubbing the product stream with water and then with caustic solution to remove entrained catalyst and some water-soluble organic compounds. Water and low-boiling-point organics produced in the oxychlorination reactor, and recycled DCE from the thermal cracking process, are removed as overhead in a light-ends distillation column, the organic components being transferred to storage prior to destruction or further processing and sale. Pure, dry DCE is taken overhead from a second distillation column and residual tars are stored prior to further fractionation, processing, or destruction with some or all of the light ends.

DCE is converted to VCM with the release of HCl by thermal cracking. Following quenching, hydrogen chloride is removed by distillation in which ethylene and acetylene are also evolved; these can be hydrogenated before being routed to the oxychlorination reactor. VCM is taken overhead from a second distillation column from which the remaining crude DCE, containing most of the impurities, is routed back to the DCE purification process. Liquid vinyl chloride is scrubbed to remove HCl before transfer to a pressurised storage vessel.

#### *Releases to air*

- Fugitive emissions of chlorinated hydrocarbons from valves, flanges, and other minor sources.
- Chlorinated hydrocarbons from storage of raw materials, intermediates, and products.
- Chlorinated hydrocarbons from reactors and columns, vacuum pumps, sampling systems, and waste-water collection and treatment systems.

Special control techniques include: high-integrity mechanical equipment double seals on pump shafts, bellow seals or similar on valves, high-quality flange gaskets; incineration of all vents with chlorinated hydrocarbons, including those from safety valves, with recovery of HCl; closed sewers.

#### *Releases to water*

- Significant organic effluent from the DCE purification section.
- Catalyst from reactors, particularly copper from fluid-bed catalyst oxychlorination units.
- Cleaning water, seal water, aqueous phase from tankage.
- Inorganic salts from water demineralisation.

Special control techniques: stripping of chlorinated hydrocarbons with air or steam, and returning to the process; removal of copper by alkaline precipitation at pH 11-12, or by electrolysis; copper catalyst in the effluent is thought to increase the possibility of dioxin emissions to aquatic media; alkaline treatment of non-volatile organics such as chloral to allow stripping or degradation.

#### *Releases to land*

- Releases of lights and heavies from the DCE purification system if not used or destroyed.
- Spent lime from VCM final purification.
- Spent catalyst from reactors.
- Sludge from settling ponds.
- Cracker decoking waste.

Special control techniques: in particular the high-temperature incineration of those chlorinated by-product streams that cannot be used beneficially.

#### **(b) Storage of vinyl chloride**

VCM is stored as a liquid under pressure in spheres or tanks. PVC manufacturing plants remote from VCM production sites receive deliveries of liquid VCM by road or rail tankers, or ship, which are normally unloaded by displacement. Storage vessels and loading lines may be vented to a monomer recovery system, and may be blanketed with an inert gas such as nitrogen. An inhibitor is often added to the vinyl chloride during storage and transport to prevent polymerisation. Potential release routes to air include vents from monomer recovery and blanketing systems, which could be routed to a vents incinerator.

There should be no significant releases to water and land.

### **2.6.3 Polymerisation of vinyl chloride**

#### **(a) Introduction**

PVC resins can be produced from vinyl chloride by four manufacturing processes: suspension, emulsion (dispersion), bulk (mass) and solution.

In the UK, homopolymer resins are produced only by the suspension and emulsion processes.

### (b) Suspension polymerisation

The suspension process comprises the batch polymerisation of vinyl chloride under pressure in demineralised water with vigorous agitation; followed by the stripping of residual vinyl chloride from the polymer resin slurry, monomer recovery and recycling within the manufacturing process, and then drying and screening of dewatered resin, and subsequent storage of PVC (Figure 2.12).

The reactor vessel is first evacuated to remove oxygen, which inhibits the reaction, then charged with raw materials. The batch is heated to reaction temperature by external heating. Thereafter the temperature of the exothermic reaction is regulated by cooling water, to produce resin grades of particular molecular weight. Agitation and suspension stabilisers control the size of the product. Polymerisation is stopped when the required conversion is reached.

Unreacted VCM, present in the water, polymer resin and vapour space above the polymer, is removed batchwise either in the reactor vessel, a separate holding tank, or a stripping column by steam stripping under vacuum. It is then transferred to a monomer recovery system for separation from water and inert gases, prior to being recycled to the process.

The stripped PVC slurry is passed through a centrifuge to remove most of the water before the resin is dried in a rotary or fluidised-bed dryer. This may be preceded by flash drying. After drying, the resin is screened to remove oversized particles and transferred to storage silos before being bagged or transported off-site in tankers.

#### Releases to air

- VCM from reactors, monomer recovery, and PVC stripping and drying.

- PVC particulate matter from transfer and storage.
- VCM from waste water collection and treatment.

Special control techniques: reduction of reactor opening frequency by use of anti-fouling agents and internal spray systems; displacement of reactor gas before opening; recovery of VCM from gas streams by carbon adsorption, refrigerated condensation, absorption/desorption with solvents, membranes or other techniques; high-integrity mechanical equipment for VCM duties; fabric filters to abate dust from dryers and other sources.

#### Releases to water

- Salts from water demineralisation.
- VCM and surfactants in reactor water, wash water, seal water.
- PVC in reactor water.

Special control techniques: stripping of VCM from waste water by air or steam; incineration or other treatment of stripped VCM; settling of PVC dust, possibly chemically aided; re-use of treated water for process washing.

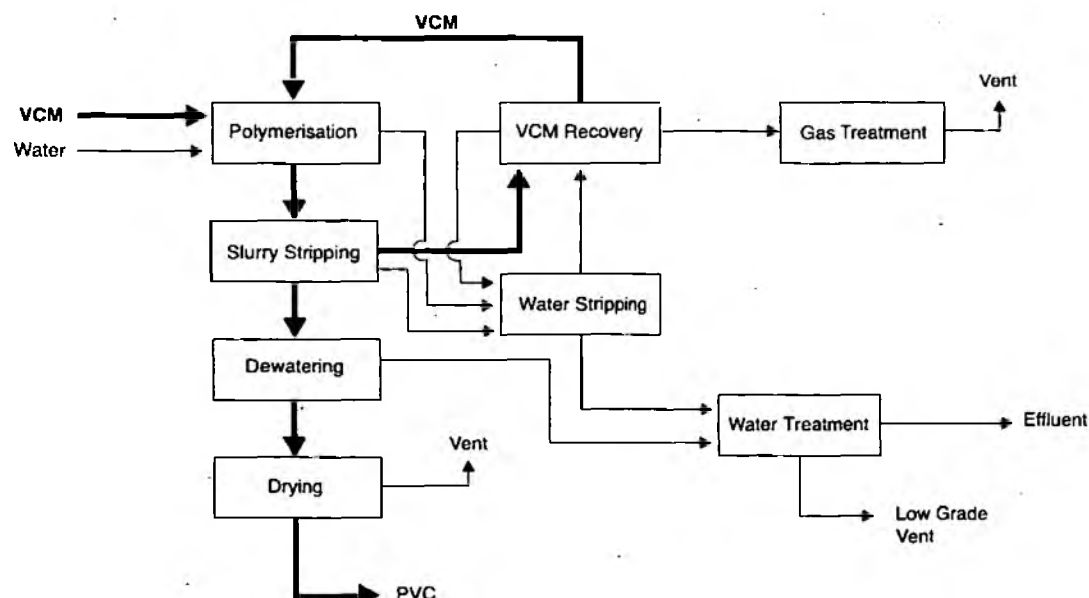
#### Releases to land

- Residual VCM with waste PVC which may contain residual VCM.

### (c) Emulsion polymerisation

Emulsion polymerisation produces resins with a smaller particle size and lower porosity than the suspension method and is carried out in water using emulsifiers and surfactants. The VCM is dispersed in the water by agitation. All the VCM can be charged initially or it can be added in stages to produce resins with a range of properties and different particle sizes needed for

Figure 2.12 PVC production: suspension





particular applications. During the polymerisation process, a portion of the PVC forms large agglomerates or 'pebbles' up to 1 cm in diameter. These will be disposed of as a solid waste containing a significant amount of entrained vinylchloride. After polymerisation, unconverted VCM (up to 15%) is removed from the latex by vacuum and steam stripping and transferred to the monomer recovery system.

Following the stripping operation the pebbles are removed before the latex is spray dried. The PVC is then screened to remove oversized particles, and is often passed through a milling operation before storage. An alternative route is to coagulate the PVC particles and separate them from the water by centrifuging or filtration and then dry using a similar system as for the suspension polymerisation route.

#### Releases to air

- VCM from reactors, monomer recovery, and PVC stripping and drying.
- Particulate matter from transfer and storage of PVC.
- VCM from waste water collection and treatment.

Special control techniques: reduction of reactor opening frequency by use of anti-fouling agents or lined reactors, though this is technically harder than for suspension PVC, plus purging before opening; stripping in reactor or, in an external batch or continuous stripper; incineration of vents containing VCM..

#### Releases to water

- PVC, surfactants and VCM from process waste water.

- Inorganic salts from water demineralisation.

Special control techniques: collection of stripper condensate, VCM recovery condensate, wash water and seal water for treatment in a water stripper; removal of very fine PVC particles by coagulation techniques.

#### Releases to land

- Residual VCM associated with waste PVC.
- Polymer from reactor cleaning operations.

The properties of PVC can be modified by copolymerising the VCM with a wide range of other monomers, of which only a few, such as vinyl acetate and the olefins, are of commercial importance. Co- and terpolymers are manufactured in similar processes to those used for the homopolymer. The releases from these processes will be similar.

### 2.6.4 Styrene

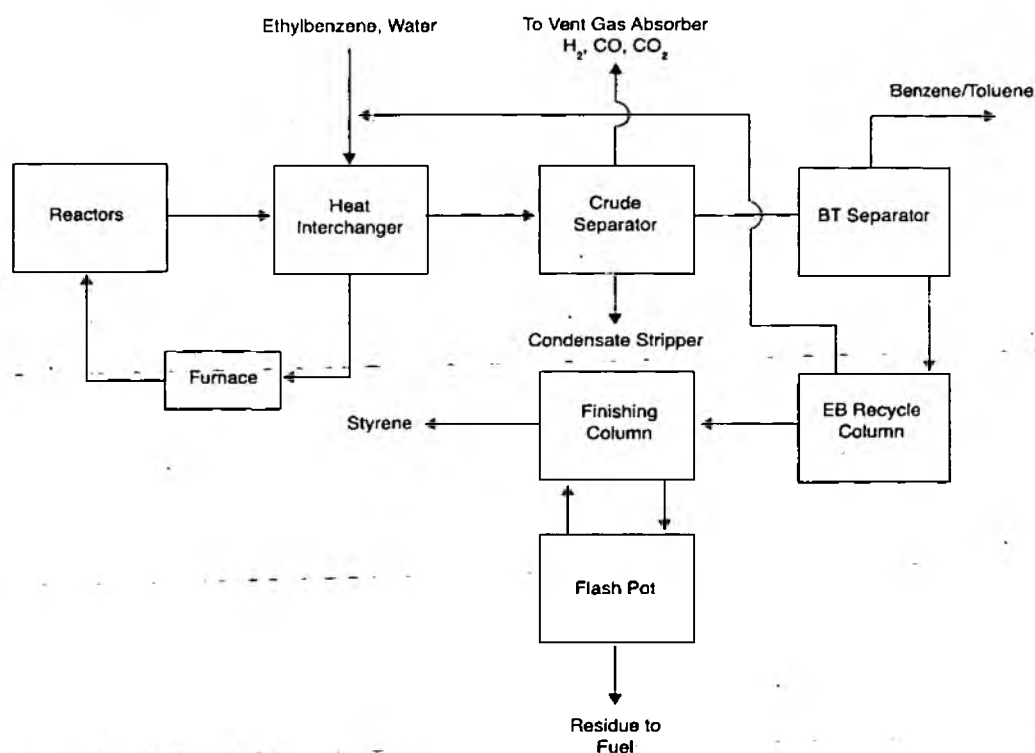
#### (a) Introduction

This section and the next section cover the manufacture or recovery of styrene; and any process for manufacture involving the use of styrene other than a process for manufacture of products containing glass fibre.

#### (b) Styrene manufacture

The majority of styrene is manufactured in a two-stage process comprising the catalytic alkylation of benzene with ethylene to produce ethylbenzene (EB), followed by the catalytic dehydrogenation of EB to produce styrene (Figure 2.13).

Figure 2.13 Manufacture of styrene: ethylbenzene dehydrogenation



Ethylbenzene production is discussed in Section 2.2.4.

A number of different routes exist for the manufacture of styrene monomer, but currently the only two commercially utilised routes are dehydrogenation of EB and air oxidation of EB. This second process consists of oxidation of EB to ethylbenzene hydroperoxide, followed by reaction with propylene to give alpha phenyl ethanol and propylene oxide; the alcohol being then dehydrated to styrene. In the UK, styrene is currently produced solely by the catalytic dehydrogenation of EB as described below. Purified EB is vaporised, mixed with superheated steam, and fed to the dehydrogenation reactor. The catalysts are generally formulated on an iron oxide base including chromium and potassium. Reaction products are condensed and separate into two phases, water and crude styrene. Hydrogen-rich process gas is recovered and used as fuel in the steam superheater and process water is normally purified in a stripper and recycled to the boiler. Crude liquid styrene, consisting primarily of styrene and EB with traces of toluene, benzene and tars, is transferred to storage.

Crude styrene is purified using low-temperature vacuum distillation in conjunction with sulphur- or nitrogen-based inhibitors to minimise polymerisation of vinylaromatic compounds. This process recovers benzene, EB and toluene. Toluene is normally sold, benzene returned to the EB alkylation reactor and EB recycled to the reactor feed. Tars are removed as distillation column residues. Purified styrene is mixed with inhibitor and transferred to storage tanks. In some facilities, an EB/benzene/toluene stream is separated from the crude styrene initially and processed separately.

#### *Releases to air*

- Benzene, toluene, EB, styrene.
- Hydrogen from catalyst preparation.
- Benzene, EB from distillation processes;
- styrene monomer from storage tanks; and
- EB, benzene, toluene and styrene releases from the purification process.

#### *Releases to water*

- steam condensate containing EB, benzene, toluene and styrene.

#### *Releases to land*

- residue from distillation columns;
- sulphur or nitrogen based residues from styrene purification; and
- spent catalyst.

## **2.6.5 Polymerisation of styrene**

### **(a) Introduction**

Three grades of polystyrene are produced in the UK: crystal (general purpose), high impact (HIPS) and expandable polystyrene (EPS).

### **(b) Production of general purpose polystyrene and HIPS**

Polystyrene is continuously produced by either the mass process or the solution process. The mass process uses no water or organic solvent whereas the solution process uses a solvent, typically ethylbenzene. The solution process is the significant process in the UK and is described below. Styrene is steam stripped of inhibitors and blended with plasticisers and ethylbenzene and fed through a series of agitated reactors under vacuum. Initiation of the polymerisation is by heat or the addition of catalysts. After polymerisation the reactor product is passed through two devolatilisation vessels under vacuum to remove the ethylbenzene and styrene for recycling. Water is injected into the second vessel to cause foaming and then decanted from the product.

The polystyrene is pelletised in an extruder, dried and then stored.

High impact polystyrene (HIPS) is produced by a batch polymerisation process similar to the process for producing general purpose polystyrene. However, HIPS has its physical properties modified by the addition of granulated rubber to styrene in the reactor with mineral oil and inhibitor. Polymerisation takes place in the reactor with reflux under vacuum. The polymer mixture undergoes devolatilisation and pelletisation using an identical process to that used for crystal polymerisation.

#### *Releases to air*

- Styrene, toluene, EB from storage, tanker unloading and filling, vessel filling.
- Styrene monomer, EB from vacuum pumps, devolatilisation systems.
- Particulate matter from product drying and handling.

#### *Releases to water*

- Styrene monomer in effluent from devolatilisation systems.

- Decanter effluent.

#### *Releases to land*

- Polystyrene residue from the separator following devolatilisation systems.
- Solid residue from separator.

### (c) Production of expandable polystyrene

Expandable polystyrene (EPS) is produced as small, white, spherical beads with a diameter of about 1 mm. Two main grades are produced, one suitable for food packaging, and the other (contains brominated compounds) with flame-retardant properties for use as insulation. The beads contain pentane to provide expansion properties when moulded by customers.

The suspension process is used, with batch polymerisation of styrene suspended in water. It comprises polymerisation, dewatering, drying, sieving and coating. Polymerisation is carried out in a stirred tank reactor, which is heated and cooled at the appropriate part of the cycle. Styrene, catalysts, suspension stabilising agents, buffer agents and flame retardant are added to the reactor initially and later pentane, after which the reactor is heated to 130°C. The suspension stabilising agent is either bentonite and gelatine or calcium phosphate.

The polystyrene slurry is sieved and then centrifuged to separate the beads. The waste water contains some beads, suspension stabilising agents, traces of spent catalyst and the buffer agents and passes through a series of settling tanks to remove the solids prior to disposal. The collected waste solids may be sold or disposed of to landfill. The beads are next coated with an anti-static agent and dried in a flash dryer followed by a fluidised-bed dryer. The dryer air is cleaned in bag filters before discharge to atmosphere. The collected solids may be sold as low-grade product.

After the fluidised-bed dryers, the beads are sieved into various size ranges and collected in hoppers purged with air direct to atmosphere, to prevent creation of a flammable mixture with pentane.

#### Releases to air

- Pentane and styrene from storage.
- Pentane from filling and opening the reactor and buffer vessel.
- Styrene during polymerisation in the reactor.
- Pentane from the dryers and product hopper.
- Particulate matter from product drying and handling.

#### Releases to water

- Decanter effluent.

#### Releases to land

- Solid residue from separator.

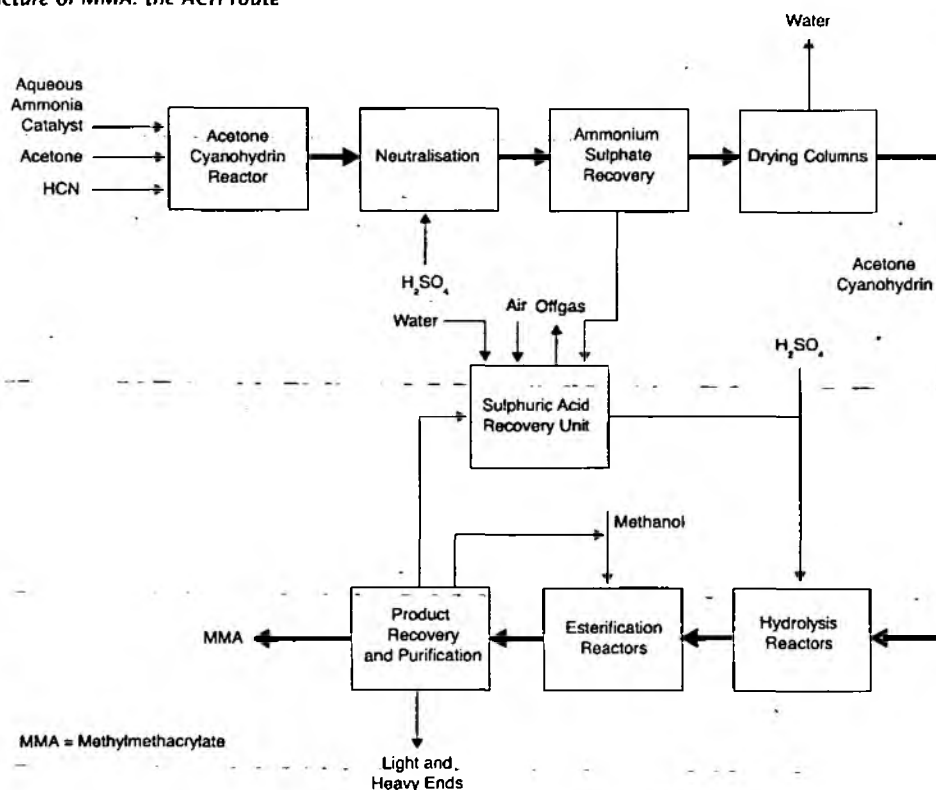
### 2.6.6 Acrylates

#### (a) Manufacture of methyl methacrylate

There are two principal routes for the production of methyl methacrylate (MMA): oxidation of  $C_4$  hydrocarbons, and hydrolysis and subsequent esterification of acetone cyanohydrin (ACH). Only the ACH route is currently used in the UK (Figure 2.14).

Methyl methacrylate is produced from acetone cyanohydrin (ACH) in a continuous process comprising three stages: amide

Figure 2.14 Manufacture of MMA: the ACH route



production, esterification and distillation.

The amide, methacrylamide sulphate, is produced by the action of strong sulphuric acid on ACH. Typically there are two reactors in series. In the first the reaction is exothermic, and so requires cooling, whilst the second is endothermic and so requires heating. Unwanted decomposition products include carbon monoxide.

The resulting amide is fed to esterification vessels where methanol and water are added. The reaction is exothermic. Steam is added to drive off organic vapour from the vessels. The liquid then passes to a stripping section for the removal of organics from the aqueous residue, the majority of which is sulphuric acid. The vapour is condensed and resulting liquid separated. The aqueous phase is returned to the esterifier, whilst the organic phase is passed to a storage tank for crude MMA. The aqueous waste streams containing sulphur may be directed to a sulphuric acid recovery plant.

The crude MMA is purified by distillation. The light fraction can be incinerated, the heavy fraction is recycled back to the esterifier, and water passes to the effluent system. A stabiliser is added to the MMA. The stabiliser in MMA needs oxygen to function and the MMA is accordingly stored under air.

#### *Releases to air*

- ④ Carbon monoxide, sulphur dioxide and organics from the amide reactor vent.
- ④ Carbon monoxide, sulphur dioxide from the condenser on the esterifier.
- Hydrocarbons from the distillation column.
- Methyl methacrylate from the storage tanks.
- Methyl methacrylate from vacuum pump discharge.

Thermal destruction should be considered for all these streams.

#### *Releases to water*

- Sulphuric acid, ammonium sulphate, sulphonated tars from the esterifier.
- Dimethyl ether, methanol, acetone, MMA, from the vacuum pump seal water and the column water fraction.

#### *Releases to land*

- Carbonaceous fouling from the esterifier vessel.
- Methacrylate polymer removed from the esterifier during shut-down.

### **(b) Manufacture of hydroxy acrylic monomers**

These are produced from the reaction of ethylene oxide and propylene oxide with methacrylic or acrylic acid in processes comprising epoxidation of the acrylic/methacrylic acid and distillation.

Crude hydroxy acrylates and methacrylates are produced in a batch process. Methacrylic or acrylic acid is charged to the reactor with the appropriate catalyst a heavy-metal based organo-metallic compound and then the ethylene oxide or propylene oxide is progressively added. The reaction is initiated by heating and, as the exothermic reaction progresses, cooling is applied to maintain the desired reaction temperature.

After reaction, when the pressure has fallen to 2 bar, the contents are transferred into a vessel where they are sparged with a mixture of nitrogen and air and vacuum treated to reduce the oxide level.

Vapours from the vacuum pump are condensed. Remaining gases, along with vapours from the sparging vessel, are vented through a water scrubber where the residual oxide is absorbed.

The crude acrylate is transferred into atmospherically vented tanks, which are aerated with small amounts of air. The crude acrylate is then purified by distillation to remove traces of the organo-metallic catalyst.

Both acrylic and methacrylic acid are stored in heated tanks. The acids are inhibited to prevent polymerisation and air is bubbled through to maintain activity of the inhibitor.

#### *Releases to air*

- Ethylene or propylene oxide from storage tanks.
- Acrylic and methacrylic acid from storage tanks.
- Ethylene or propylene oxide, acrylates from the vacuum pump.
- Ethylene or propylene oxide from charging of pre-mix vessel and reactor.

#### *Releases to water*

- Ethylene or propylene oxide in scrubber effluent.
- Ethylene or propylene oxide, acrylates in condensed steam and cooling water.
- Catalyst in distillation column effluent.

#### *Releases to land*

- Acrylates and catalyst adduct in distillation bottoms.
- Polymer from reactor and distillation column cleaning.
- Spent catalyst.

**(c) Acrylate recovery**

The recovery operation is a batch process for recovery of the methyl methacrylate monomer from cast acrylic sheets, and can be divided into three stages; depolymerisation, washing and vacuum distillation.

Scrap sheet is crushed and charged into a sealed reactor purged of air and containing an electrically heated molten lead bath. Vapours from the reactor are passed through a water-cooled condenser from which condensed methyl methacrylate is collected and pumped to storage. Any uncondensed gases are passed to a caustic scrubber and then to a carbon adsorber.

The next stage of the process is batch washing of the crude monomer with caustic solution. The aqueous layer and the MMA both contain lead.

The third step in the process is vacuum distillation. Discharge from the vacuum system is scrubbed with chilled MMA, and the residual organics from the scrubber pass to a catalytic incinerator. The distilled monomer is pumped to storage tanks, vented through an activated carbon adsorption unit. Bottoms (up to 30% of charge) from the vacuum column are drained off to a batch tank, vented through an activated carbon adsorption unit, and incinerated.

**Releases to air**

- Methyl methacrylate, lead vapour from reactor vent during recovery operation and vessel purge.
- Methyl methacrylate from vacuum pumps.
- Methyl methacrylate from storage.
- CO, CO<sub>2</sub>, NO<sub>x</sub> from catalytic incinerator.
- Particulate matter from scrap handling.

**Releases to water**

- Caustic solution, methyl methacrylate, and lead from monomer washing.

**Releases to land**

- Methacrylate polymers, and lead from the distillation column.
- Lead oxide and other metal colorants.
- Carbon waste from carbon adsorbers.

**(d) Storage of acrylates**

The principal considerations affecting acrylate storage are:

- the effectiveness of inhibitors and the storage life under various temperatures;

- flammability and combustibility; and
- toxicity.

Other considerations, including prevention of contamination, the physical and chemical properties of the monomers, their odours, and their sensitivity to environmental conditions, such as light, moisture and oxygen, are also important.

Generally, acrylates are stored at ambient temperatures. A typical inhibitor is MEHQ, which requires a small amount of oxygen to function. This means that a nitrogen blanket is not appropriate. Acrylates, particularly ethyl acrylate and methyl methacrylate, have moderate vapour pressures and potential releases from storage tanks can be significant. All acrylates are odorous; for ethyl acrylate the odour threshold is as low as 0.4 ppb. Depending upon the storage conditions, scrubbing, carbon adsorption and incineration may be considered for vent treatment.

**Releases to air**

- Tank vents.

**Releases to water**

- Loading and unloading spillages, and caustic scrubber waste water.

**Releases to land**

- Loading and unloading spillages.

**2.6.7 Use of acrylates****(a) Introduction**

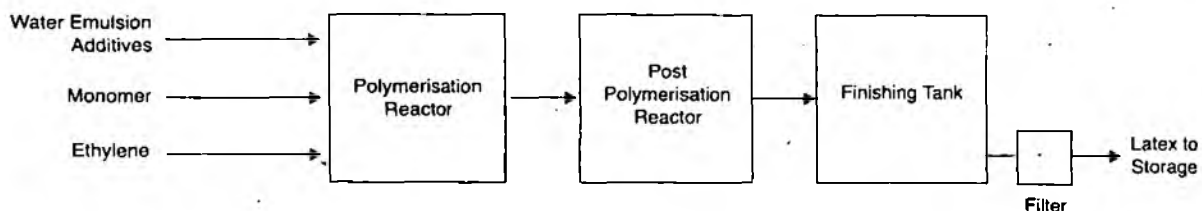
Acrylic acid esters (methyl to 2-ethylhexyl) are clear, colourless liquids with strong acid odours; multifunctional speciality acrylates are more viscous. Acrylate monomers undergo vinyl-type emulsion polymerisation in water or solvents. Processes used to produce acrylate polymer compounds, or acrylate solution polymers, are very similar, differing only in size of operation and additives used. Most reaction systems are batch but there are some continuous ones.

**(b) Water-based acrylic emulsion polymers**

The acrylate monomers and other monomers such as styrene, vinyl acetate, acrylamide, methacrylamide, acrylic and methacrylic acid, and acrylonitrile are charged either to a pre-mix vessel or directly to a reactor where they are mixed with water stabilisers and additives (Figure 2.15). Where a pre-mix vessel is used the reactor is normally equipped with some form of heating. Either a closed or refluxed reactor is used. Some reactors vent to caustic scrubbers, generating a waste water stream containing spent caustic and sodium acrylate.

Following polymerisation, the material is filtered and sent to storage. Sometimes an intermediate vessel is used before

Figure 2.15 Simplified emulsion polymerisation process



filtration for balancing, additions or dilution. Surfactants may be used to prevent coagulation and subsequent blocking of the filters.

#### Releases to air

- Monomers from pre-blend tanks, reactor charging, reactor operation, storage tanks and drum filling.

Special control techniques: incineration of VOC streams from storage tanks and process vessels.

#### Releases to water

- Monomers, acrylate polymers, surfactants from reactor wash-downs and process water, filter washings.
- Spent caustic solution containing acrylates, sodium acrylates from scrubber.

Waste water recycling is often practised.

#### Releases to land

- Off-specification polymer, often reworked.
- Polymerised solids from reactor fouling.
- Polymer residues from filters.

#### (c) Solvent-based acrylic polymers

The solvent-based process is a batch process similar to that for water-based emulsion polymers. The acrylate and other monomers are pre-mixed with stabilisers and additives, and drip-fed into a reactor containing solvent, which can be heated or cooled. Commonly used solvents include xylene and toluene. The vessel is typically fitted with a water-cooled condenser venting to atmosphere.

The product is filtered before being transferred into drums. Sometimes an intermediate vessel is used before filtration for balancing, additions or dilution. For some products, the solvent may be stripped off, using vacuum stripping, and recycled back to the process.

Typically, the vessels will only be washed out between batches using different solvents. The vessel is first rinsed with solvent, which is reclaimed by distillation, and then boiled out with caustic, the spent caustic being discharged into the plant waste water system.

#### Releases to air

- Monomer and solvent from pre-blend tank, reactor charging, reactor operation and wash-down and storage tanks.

#### Releases to water

- Monomers, acrylate polymers, surfactants from reactor wash-down, process water, filter washings.
- Spent caustic solution containing acrylates, sodium acrylate from scrubber.
- Spent caustic from reactor wash-down.
- Solvents.

#### Releases to land

- Polymerised solids from reactor fouling.
- Polymer residues containing solvent from filters.

#### (d) Manufacture of acrylic moulding powders

Acrylic moulding powders are produced using emulsion and suspension polymerisation techniques. The process involves batch polymerisation of methyl methacrylate with other comonomers that are mixed in a preparation vessel prior to being charged to an autoclave.

The autoclave has provisions for both heating and cooling and a typical charge consists of deionised water, poly(methacrylic acid), phosphate buffer and other minor additives. Polymerisation is initiated by heating. The exothermic reaction is controlled by cooling of the vessel. Overpressure may be caused by loss of stirring or cooling.

Gases from the autoclave are removed via a vacuum system, which discharges to atmosphere. After polymerisation the product is sieved and stored as a slurry.

The slurry is centrifuged to remove water and unreacted organics, and then re-slurried with water. This slurry is dewatered and dried in a second series of centrifuges, which discharge the product to a rotary steam-heated dryer. The product is cooled, sieved and packed or routed to storage bins.

*Releases to air*

- Methyl methacrylate, acrylates from storage, pre-blend vessel, autoclave, and vacuum system.
- Particulate, acrylate monomers from dryers, filters.
- Particulate matter from product storage hoppers.

*Releases to water*

- Acrylate monomers and polymer from autoclave wash water, slurry wash water.
- Acrylate monomers and phosphates from centrifuges.
- Water seal containing acrylate monomer from liquid ring vacuum pump.
- Warm wash water containing monomer and polymer from vessel cleaning after each campaign.

*Releases to land*

- Polymer fouling from autoclaves.
- Polymer from centrifuges, settling tanks.
- Polymer, dust from filter residues.

**(e) Manufacture of poly(methyl methacrylate)**

Poly (methyl methacrylate) (PMMA) is produced from methyl methacrylate in a batch process. PMMA is generally combined with additives, which are typically colourings such as inorganic compounds of iron, titanium and cadmium.

The monomer is heated and charged to the reactor. Catalyst is added and, once the syrup has reacted sufficiently, air pressure is used to transfer the hot monomer/polymer mixture via a cooler to the stirred blending vessel. Here colouring agents are added. Lines are back-flushed with monomer to prevent build-up.

The mixture is transferred to an evacuator vessel where vacuum is drawn to remove entrained gas bubbles, before being transferred, via a filter, into the casting chamber. Here PMMA sheets are cast between glass plates sealed with a flexible gasket and placed in the polymerisation oven. The PMMA is heat-treated to achieve polymerisation. Both the glass plates and PMMA sheets are rinsed using treated demineralised water and detergents. Wash water goes to the waste water collection system. The PMMA is air-dried, inspected for imperfections then wrapped in polythene and stored. Vessel washing residues are sent for recovery.

*Releases to air*

- Methyl methacrylate from storage, vessel filling, blender, evacuator and vacuum pump.

*Releases to water*

- Waste water from heating, cooling, washing, rinsing operation (pH, sodium-based corrosion inhibitor, biocides).
- Acid and caustic from water demineralisation operation.
- Seal fluid from vacuum pumps.

*Releases to land*

- Particulate matter (dust) from cutting, trimming of sheets.
- Methyl methacrylate and PMMA from overmake, drips and spills.

**2.6.8 Nylon salt**

Nylon salt is produced by mixing the two monomers, hexamethylenediamine (HMD) and adipic acid, together in an aqueous solution in a stoichiometric ratio. The resultant product is an aqueous solution of the nylon salt of approximately 50 wt% concentration.

A saturated aqueous solution of adipic acid is fed into a dissolver unit, and demineralised water and half the required HMD is added. The reaction is instantaneous and slightly exothermic.

The product is transferred to the first reactor vessel where the majority of the remainder of the HMD required for neutralisation is added. The reactor is operated under vacuum and the heat of reaction is removed by water evaporation. This water contains some HMD and is condensed and recycled back to the reactor.

The nylon salt from the first reactor is transferred to a second reactor, also operating under vacuum, where small quantities of HMD are added under pH control. The resultant nylon salt is then pumped to storage where either HMD or adipic acid is added as necessary to adjust the pH to the desired level. This determines the adipic:HMD ratio and hence the eventual nylon polymer molecular weight.

A filtration step is often required to remove solid impurities (usually iron corrosion products) from the salt solution. Storage of nylon salt is carried out under a nitrogen blanket to prevent discoloration of the product by air oxidation. Stabilisers such as hydrazine are also added to improve the stability of the salt and prevent colour degradation.

*Releases to air*

- Vents from feedstock vessels.

*Releases to water*

- Filter washings.

### Releases to land

- Filter aid and cake.

### 2.6.9 Nylon polymers

Nylon polymers are produced by polymerising nylon salt. The properties of the nylon polymer can be modified to suit end-use requirements by the addition of small amounts (ppm levels) of various additives such as copper acetate, potassium iodide, borax, topanol, sodium hydrogenphosphite, copper bromide etc. Titanium dioxide is often added (less than 2 wt%) as a whitener to fibre grades and caprolactam can be added (3–9wt %) to make a copolymer.

A typical production process involves the following basic steps, which are common to all nylon polymerisation processes, although some variations do occur depending upon the end-use of the nylon polymer.

Nylon salt solution is heated and transferred to a measuring vessel where additives are added. This mix is then evaporated to increase the salt strength. The off-gases, which contain trace quantities of HMD, are condensed and disposed of. After completion of the evaporation cycle the mix is transferred to an autoclave unit.

If caprolactam is to be added it is done so at this stage before polymerisation occurs. Polymerisation processes have a range of process cycles, but essentially involve applying heat to typically 300°C at elevated pressures (typically 18 bar) to remove the remaining water content of the nylon salt as well as the water of reaction generated by the polymerisation reactions. The water driven off generates a waste stream. Air is excluded to prevent oxidation of the polymer.

At the completion of the polymerisation reaction when the properties of the mix are acceptable, the molten polymer is extruded from the autoclave through a die. Depending upon whether the final product (eg fibre) is being produced directly or whether nylon chips are being produced as an intermediate stage, the hole size of the die is varied. In the latter case strands several millimetres in diameter are extruded and chopped into chips, which can then be easily handled and transported to any subsequent spinning or moulding stage.

Off-specification product produced in the manufacturing process can usually be blended into lower-grade products with less critical specifications, thus minimising the generation of solid waste.

### Releases to air

- Feedstock vapours from storage.
- Off-gases from the evaporator and condensers in the polymerisation section.
- Off-gases from the die cleaning scrubber.

### Releases to water

- Waste streams from the condenser systems.
- Waste streams from the scrubber system.

### Releases to land

- Off-specification product.

### 2.6.10 Acrylic fibres

Acrylic fibres, which consist of polyacrylonitrile (PAN), can be produced either by the heterogeneous polymerisation of acrylonitrile in solution or by solution, polymerisation. The latter process allows the acrylic fibre to be spun directly from the polymer solution whilst the former requires the separation and drying of the solid polymer before it is redissolved prior to spinning and is therefore a more energy-intensive process.

Two principal spinning processes are used. In dry spinning an organic solvent such as dimethylformamide, which has a low volatility and can therefore be easily recovered, is used to dissolve the polyacrylonitrile. The solution is forced through a spinneret and the solvent evaporated using hot air and the strands allowed to form. In wet spinning the polyacrylonitrile fibres emerge from the spinneret into a water bath. The fibres coagulate and the solvent diffuses into the water. A solvent recovery plant is required to recover the solvent.

Commercial polyacrylonitrile contains various additives designed to modify its properties and also minor amounts of unreacted acrylonitrile. These additives can include neutral monomers such as methyl acrylate, methyl methacrylate and vinyl acetate to copolymerise with the acrylonitrile and increase the stability of the polymer in various solvents. Other additives include ionic monomers, halogen-containing monomers and compounds such as sodium styrenesulphonate, which provides dye sites, enhancing dyeability.

The choice of process is largely determined by the end-use of the fibres. Acrylonitrile is moderately water-soluble but the polymer is insoluble in both acrylonitrile and water. This makes aqueous heterogeneous polymerization, either batchwise or continuous, a natural choice where the polyacrylonitrile polymer is to be isolated prior to redissolving and spinning. In a typical continuous process, monomer, water and initiator are fed to a continuously stirred overflow reactor. The slurry of polymer, water and unreacted monomer is filtered or centrifuged, the polymer washed and dried, and the monomer is recovered from the filtrate and returned to the reactor.

In the UK a high-quality fibre is required that is clean and white and this requirement determines the choice of the continuous solution polymerisation process. The polymer is wet spun directly from solution. The fibre produced typically comprises 90% acrylonitrile, 6–9% methyl acrylate and about 1% acidic monomer.

A high-quality fibre requires an acrylonitrile feedstock that is free of the impurity oxazole. It is therefore necessary to purify the acrylonitrile by passing it through an ion exchange resin.



This process generates some loss of acrylonitrile when the resin bed is periodically regenerated with dilute sulphuric acid.

The reaction stage consists of a continuous feed of acrylonitrile, monomers, dye sites, initiators, colour improvers and solvents, such as sodium thiocyanate solution, to the reactor. Unreacted acrylonitrile in the polymer is removed by multi-stage evaporation (demonomerisation) prior to the spinning stage, so that acrylonitrile vapour concentration in intermediate storage facilities and at the spinning bath stage is acceptable. The condensed vapours from the initial evaporation stages are recycled to the reactor, whilst those from the latter stages are often waste streams requiring treatment.

The spinning stage extrudes the polymer solution through a spinneret and into a counter-current washing stage in which water washes the solvent from the fibre. The wash liquor is passed to a solvent recovery process.

The fibre is steam stretched, water washed, dyed, a surface lubricant added, dried, an anti-static agent added, crimped and packaged for sale. Vapours are released during these processes by evaporation from the surfaces of the various liquid baths and from the dryer exhaust.

The solvent recovery process concentrates, using a multi-stage evaporator, the weak solvent solution from the washing stage so that the solvent can be recycled. Evaporated water containing traces of organic impurities is condensed and sent for disposal. The concentrated solvent contains impurities that must be removed before recycle and these require a further three recovery stages – sulphate removal, iron removal and the removal of soluble impurities.

Sulphate removal is by the addition of barium carbonate to precipitate barium sulphate, which can then be filtered. Iron removal is by an ion exchange resin column. Regeneration of the column generates a waste stream.

Removal of soluble impurities is achieved by the Solvex process. The Solvex process consists of an initial absorption column where the weak solvent (sodium thiocyanate solution) is contacted with diisopropyl ether and sulphuric acid to extract a top ether phase containing the purified thiocyanate as thiocyanic acid and a bottom waste aqueous phase.

The purified sodium thiocyanate is regenerated from the ether phase by contacting with caustic soda solution. This creates an ether phase that can be recycled and an aqueous solvent phase which, after air stripping to remove the ether, is suitable for recycle to the reaction stage.

#### *Releases to air*

- Monomers from reaction and demonomerisation systems.
- Monomer, fibre and solvent from spinning sections and fibre treatment.
- Monomers from solvent recovery.
- Ether from sodium thiocyanate purification.

#### *Releases to water*

- Streams containing monomers from solvent recovery plants, ion exchange plants, and demonomerisation.
- Streams from solvent purification.
- Effluent from dye baths and rinses.

#### *Releases to land*

- Spent ion exchange resins.
- Streams from solvent recovery plant.

### **2.6.11 Acrylonitrile, butadiene, styrene copolymers**

There is a wide range of these copolymers. The production of nitrile rubber is given as an example of the process type.

Nitrile butadiene rubber (NBR) is produced by copolymerisation of butadiene and acrylonitrile. Different grades are produced by varying the acrylonitrile: butadiene ratio. Complete conversion of monomer to polymer does not occur and so monomer recovery and product purification/processing stages are required.

The initial stage of the process involves copolymerising acrylonitrile and 1,3-butadiene to give a homogeneous copolymer by free-radical polymerisation. Water and an emulsifying agent are added along with modifiers, such as chain transfer agents, and inhibitors to control the extent of polymerisation.

NBR may be produced by either a continuous or batch process.

In the batch process the polymerisation typically occurs in one vessel and then the product is transferred to a second vessel where monomers are recovered by vacuum treatment. Butadiene comes off initially and can be recovered and recycled. Most of the acrylonitrile is then removed but some is left to prevent polymer degradation which would result in the production of a solid waste and fouling of the process vessels. In the continuous process several continuous stirred tank reactors are used in series with the inhibitor and stabiliser added to the last reactor. A flash vessel is used to remove butadiene. The pressure is then lowered and the product mix steam stripped to remove the acrylonitrile. The overheads are condensed to recover the volatile monomers from the gaseous stream. Water, acrylonitrile and butadiene can be recovered.

The product mix in latex form can be either sold or sent forward for further processing as required. Acrylonitrile will be vented from this intermediate storage and requires treatment to minimise releases.

For further processing the latex is transferred to a coagulation vessel where inorganic salts and small quantities of mineral acids are added as coagulating agents. After a precipitating agent has been added, dilute caustic soda is commonly used to remove the emulsifying agent.

The precipitate of nitrile latexes is washed, filtered, washed again and then continuously fed to a dryer. The water washings will contain small quantities of acrylonitrile and fines (non-coagulated polymer), which are removed.

Drying the coagulated solid nitrile rubber will release some acrylonitrile. Drying methods employed include drying drums, band dryers and drying screws. Powder, such as talc or magnesium stearate, can be used to avoid agglomeration of the material and adherence to dryer surfaces. The choice of drying method depends largely on the properties required of the final nitrile rubber.

#### Releases to air

- Monomer in vents from reactor, vacuum systems, vent treatment systems.
- Monomer and particulates in vents from powder handling systems and dryer.

#### Releases to water

- Releases from vent treatment equipment.
- Monomer and polymer in latex wash water.

#### Releases to land

- Polymer from vessel cleaning.

### 2.6.12 Polyethylenes

There are several types of polyethylene produced, of which the main groups are:

- Low-density polyethylene (LDPE);
- Linear low-density polyethylene (LLDPE); and
- High-density polyethylene (HDPE).

For each type of product there are several licensed processes available. Considerable technical development by producers continues globally, with new catalysts and processes aimed at

providing attractive properties to customers and consumers. Awareness of emissions of ethylene has gained in recent years because of its relatively high photochemical ozone creation potential, in spite of being substantially non-toxic.

Comonomers (usually olefins) are used for some products, but this does not substantially affect the environmental profile of the processes.

#### (a) LDPE processes

LDPE is produced by polymerising ethylene using free-radical initiators such as oxygen or organic peroxides. Operating pressures are high, at 2000-3000 bar, and cooling is used to keep temperatures below 350°C at which ethylene might decompose. Processes fall into two categories: autoclave or continuous tubular reactor processes. A characteristic feature of older LDPE plants is the decompression, or 'decomp'. These occur when ethylene decomposes in hot spots and the reactor vents violently. Computerised control minimises the occurrence of this phenomenon.

A typical LDPE block diagram is shown in Figure 2.16.

#### (b) LLDPE/HDPE processes

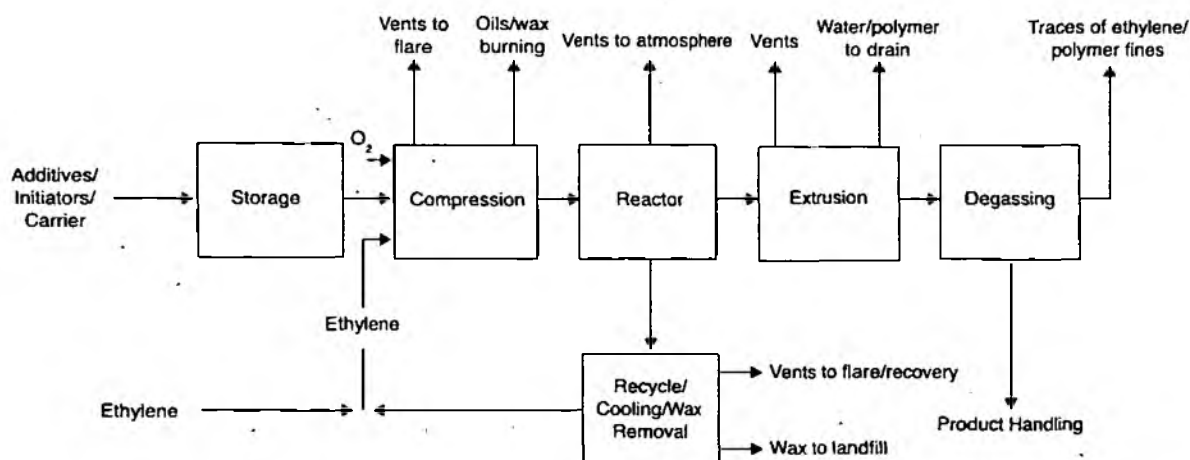
Several LLDPE processes are also capable of producing certain grades of HDPE on a swing basis. Low-pressure conditions are employed, with Ziegler Natta catalysts or supported heavy-metal oxide catalysts. Metallocenes, a new class of Ziegler Natta catalysts, have been the focus of much of the recent technological development. Most modern catalyst systems are usually sufficiently active to avoid the need for de-ashing.

There are three basic types of process: gas-phase, solution, and slurry. The solution and slurry processes employ hydrocarbon solvents and tend to have more purge streams than gas-phase plants. These include waxes, solvent purges, and waste-sieve materials.

#### (c) HDPE process

Processes dedicated to HDPE are usually intended to produce high-molecular-weight material suitable for blow moulding.

Figure 2.16 LDPE production



Both slurry-phase and gas-phase processes are available.

#### *Releases to air*

- Purges of feedstocks or solvents, or the products of their combustion.
- Hydrocarbons from raw material storage, degassers, extruders, dryers and hoppers.
- Fugitive losses of feedstock and solvent hydrocarbons.
- Vents from catalyst preparation systems, possibly with organo-metal content.
- Vents at high pressure (LDPE).

Special control techniques: computerised control on LDPE plants to reduce occurrence of decompressions; recycle of purge streams for process use or fuel; catalytic oxidation of vents from degassers, etc; underwater face cutters; use of high-integrity equipment and fittings where gases and volatile liquids are handled, plus leak detection and repair (LDAR).

#### *Releases to water*

- Wash water or pellet system overflow.

#### *Releases to land*

- Off-specification product.
- Waxy or heavy liquid purges.
- Organo-metallic compounds from catalysts.

Special control techniques: beneficial use of hydrocarbon residues, including as fuel; use of modern high-activity catalysts.

### **2.6.13 Polypropylene**

Polypropylene is produced by polymerising propylene. Homopolymer grades are produced from propylene alone, while copolymers incorporate another monomer such as ethylene. Random copolymer and high-impact copolymer supply different market needs.

The three main types of polypropylene process are gas-phase, bulk, and slurry. The catalysts have been improved in four generations of development, and de-ashing should not be required on any modern process. A lower-grade polypropylene, termed atactic, is typically produced in small quantities from the slurry process, but can usually be sold for adhesive or other uses.

Examples of the three process types are described below.

#### **(a) Bulk Process**

This uses a continuous single-stage polymerisation reaction to produce homopolymers only. Liquid propylene is dried using

molecular sieves and treated with copper and zinc oxide catalyst. The catalyst is prepared under high-purity nitrogen. Liquid propylene and small amounts of catalyst components and hydrogen are metered into the polymerisation reactor where the solid polypropylene particles are formed as a suspension in liquid propylene. There are no significant by-products from the reaction. The liquid propylene is evaporated from the propylene-polymer mixture and the polymer is collected by cyclone and bag filter systems. Polymer powder is nitrogen stripped and then fed to the extrusion unit.

#### *Releases to air*

- Propylene particulate matter from vents (on dust extraction, extruder, extruder extract).
- Propylene/propane from powder vessel vent, which is generally thermally incinerated.
- VOCs from extruder extract vent.
- Polymer dust from granulate transport air.
- Thermally incinerated bleed streams for which no further recovery or use is practicable.

#### *Releases from water*

- Polypropylene from granulate water tank overflow, extrusion floor washings.
- Hydrocarbons from molecular sieve regeneration liquid.
- Inorganic salts from vents scrubbing and/or wash waters.

#### *Releases to land*

- Spent molecular sieves from olefin pre-drying.
- Polypropylene powder from powder vessel clean-out.
- Polypropylene additives from vacuum cleaning of solids.
- Copper and zinc oxide from spent catalyst packs.

#### **(b) Gas-phase process**

Propylene is dried over aluminium oxide and polymerised in a gas-phase reactor, using a catalyst and activator. Catalyst is pre-treated with propylene in heptane. Propylene and ethylene are used if a copolymer is required. Polypropylene powder from the reactor is separated and deactivated using nitrogen, isopropyl alcohol and steam. The deactivated powder is transported to granulation under nitrogen, mixed with additives, extruded and chopped into granules under water.

#### *Releases to air*

- Propylene, propane, heptane and pentamethylheptane from splitter purge vents and intermittent gas vents.
- Hydrogen chloride from deactivation vent.

**Releases to water**

- Sodium hypochlorite, polypropylene from aqueous waste.
- Nalfloc from cooling tower.

**Releases to land**

- Aluminium oxide from spent catalyst.
- Polypropylene from process waste.
- Hydrocarbons from oil/water separator drainings.

**(c) Slurry process**

In the slurry process, a hydrocarbon diluent such as n-heptane is used. The reaction conditions are modest, at 60°C, 12 bar. Catalyst and co-catalyst slurries are prepared with solvents and metered continuously to polymerisation reactors.

**Releases to air**

- Purges of feedstocks or diluent, or products of their combustion.
- Hydrocarbons from raw material storage, degassers, extruders, dryers, products hoppers.
- Fugitive losses of feedstock and diluent hydrocarbons.
- Vents from catalyst preparation.

**Releases to water**

- Wash water or pellet system overflow.

**Releases to land**

- Atactic polypropylene (if not sold).
- Off-specification polypropylene.
- Heavy ends from solvent recovery.
- Organometallic compounds.

Special control techniques for polypropylene processes: recycle of purge streams to process plant or for fuel use; catalytic oxidation of other significant vents; use of high-integrity equipment and fittings where gases and volatile liquids are handled, with LDAR; underwater face cutters; beneficial use of hydrocarbon liquid or solid residues, including as fuel; use of modern catalysts to avoid de-ashing and to minimise atactic formation.

**2.6.14 Resins**

Resin is a term used for a wide range of organic polymers including some described under copolymerisation of vinyl chloride and use of acrylate.

Resins are typically manufactured in essentially closed batch reactors operating at temperatures up to 300°C and pressures ranging from vacuum up to 10 bar, although where low-boiling monomers such as butadiene, ethylene and vinyl chloride are used the pressure can be up to 100 bar.

The monomers are charged either to a pre-mix vessel or directly to the reactor. If a solvent or water is being used, then this is normally charged to the reactor first. Additives such as catalysts/initiators and stabilisers are fed to the reactor and the reaction started. As the reaction proceeds further additions of all raw materials are made, although if it is a fusion reaction all the monomer is added initially. Some reactor vents are caustic or water scrubbed.

After the reaction has finished, or been stopped, the charge is often fed to an intermediate vessel for dilution, further additions or blending. The product is either filtered to produce the liquid form or dried by such means as a belt flaker to produce the solid form.

Polyester/alkyd products use vegetable oils, fatty acids, polyols and acids as monomer raw materials. The alkyds can be modified with a variety of compounds.

Epoxy ester products use fatty acids and epoxy resins (usually reaction products of epichlorhydrin and diphenylolpropane) as monomer raw materials.

Rosin-based resins use rosins, polyols, anhydrides, alkaline-earth oxides and phenols as monomer raw materials. Polyamides use acids and amines as monomer raw materials. Amino resins use acids, alcohols, urea and amines with formaldehyde as monomer raw materials.

Phenolic resins use phenols, cresols, xylenols and formaldehyde as monomer raw materials.

**Releases to air**

- Solvent and monomers from storage, reactor systems, intermediate vessels, filtration, solidification equipment, and product packing out.

**Releases to water**

- Solvent polymer and monomer from reactor and vessel cleaning, and filtration.
- Spent scrubbing liquor containing solvent and monomer products.

**Releases to land**

- Filtration residue and media.
- Polymerised solids from reactor fouling.
- Non-recyclable gelled resins.

### 3 Best available techniques for controlling releases

#### 3.1 Introduction

This section covers techniques for controlling releases that are common to many processes or are considered to be general in their application, ie are aspects of overall management of a works to minimise releases to the environment.

The standard techniques for pollution abatement are outlined in various reference sources including:

- Air Pollution Advisory and Review Group<sup>(24)</sup>, reports;
- BAT Review Reports on Pollution Control;
- Environment Agency Guidance Notes; and
- Environmental Technology Best Practice Programme (ETBPP). Good Practice Guides<sup>(25)</sup>.

These techniques need to cover releases from raw materials reception/storage, internal transportation, processing, waste materials internal transport and storage pending disposal.

The processes should be designed and operated in such a way that the substances released have the minimum impact on the environment. As a general principle the Inspector should be looking for evidence that the releases of prescribed substances will be prevented, or minimised and rendered harmless, and that releases of other potentially harmful substances will be rendered harmless: this should then be confirmed by conditions in the Authorisation. Since the priority is to prevent releases, emphasis should be placed on the avoidance of processes and abatement techniques that create wastes.

Prevention, minimisation and recycling procedures<sup>(26,27)</sup> should be applied whenever possible, within the criteria for BATNEEC and BPEO.

The Inspector should be satisfied that an applicant has reviewed all available options and has demonstrated that the selected combination of primary process and abatement equipment represents BATNEEC, and that the concept of BPEO is satisfied.

More details of the methods available for preventing or reducing releases are listed in Research Report No P181<sup>(28)</sup>. This contains references to techniques used on different processes in the UK and internationally. The most important techniques include, but are not restricted to, those given below.

#### 3.2 Management techniques

Effective management is central to environmental performance and is an important component of BAT. It requires an actual commitment to establishing objectives, setting targets, measurement and revision according to results. This systematic approach may be aided by the achievement of management

standards such as ISO 14001 and EMAS<sup>(29)</sup>. The following sections provide information on the main types of management technique.

##### 3.2.1 Senior management commitment

The commitments made by companies that sign up to the 'Responsible Care'<sup>(30)</sup> or similar initiatives provide a good framework for the implementation of management techniques. The key aspects of this initiative, which companies should be committed to through their senior management, and which they should be able to demonstrate they are applying, are that:

- all health, safety and environmental impacts of activities, products and processes have been identified and considered;
- there is a commitment to conform with statutory regulations as a minimum and work with authorities to develop and implement measures where needed;
- employees and contractors are aware of the commitment and are involved in its delivery; and
- they are open with information both inside and outside the organisation.

A company might not be a formal signatory to this initiative but could still be expected to be aspiring to its principles.

##### 3.2.2 Organisation and responsibility

There should be a clear structure for managing environmental issues in general and ensuring compliance with the Authorisation in particular. This should be fully integrated with the process operator's wider company and site decision-making systems. Many sites have a management committee and it would be expected that the environment is represented on it and discussed at regular intervals.

There should be a clear contact point for the IPC authorisation; usually this requirement can best be met by having a single point contact. This should be seen as clarifying the interface between Agency and process operator. It should not reduce the responsibilities of other members of staff for ensuring compliance with the Authorisation.

The environmental performance of the process is highly dependent on the attention and awareness of the process operator's staff. They should be aware of this and their role in this performance made clear. The company should reinforce the message that environmental protection matters to the company. One way to do this is to have environmental performance as a part of annual performance assessments.

Incidents have occurred in the past as a result of poor communication among operations staff during shift changes and maintenance or other engineering work. Specific procedures should be in place to avoid such problems.

The planning and scheduling of batches can influence waste production and the company operating the process should be able to show that these opportunities have been considered and, where favourable, implemented.

The overall environmental performance of the process should be monitored and the results should be considered on a regular basis and form part of the management assessment process. Environmental performance indicators (EPIs) could be used for this purpose, although the potential difficulties of deriving them for rapidly changing batch operations should be recognised.

A contingency plan should be in place which identifies the potential types of incident that could occur and provides clear guidance on how they will be managed and who is responsible. In some circumstances these will need to be notified to the Agency as a condition of the process Authorisation and these must be clearly defined. Procedures should be in place to identify, respond to, and learn from all complaints and incidents.

### 3.2.3 Maintenance

A programme of preventive maintenance should be in place and recorded, coupled with diagnostic testing where appropriate.

Records of process performance should be available and used to monitor slow changes in releases that may signal the need for maintenance.

All staff should be aware of the role they can play by maintaining vigilance, for example, in relation to process upsets and leaks, and appropriate procedures should be in place to encourage staff involvement.

A procedure should be in place to authorise modifications and to undertake checks after modifications before process start-up.

### 3.2.4 Process control

The operator should be able to demonstrate that the process is being adequately controlled; in many cases this will involve the use of a computer-based system with facilities to ensure control in emergency situations.

As noted above there should be records of production and a procedure in place to ensure that they are subject to periodic review.

### 3.2.5 Waste minimisation

Waste minimisation audits should be conducted periodically to a defined programme. The Institution of Chemical Engineers, amongst others, has issued guidance on waste minimisation<sup>(10)</sup>, whilst a number of Waste Minimisation Clubs have been set up, eg Aire and Calder.

The active participation of staff should be encouraged in these initiatives with recognition given to those who identify waste minimisation improvements.

There should be active monitoring of materials throughput and mass balances should be available for processes. Monitoring should include water, power, heat and solvent use.

### 3.2.6 Design

The environmental implications of a new process or product should be considered at the earliest stages of the project and should continue to be reviewed at regular intervals thereafter. This is the most cost-effective time to introduce improvements in overall environmental performance. There should be evidence that alternative process options were considered and assessed. It should be possible to maintain an audit trail of the design and decision-making process.

### 3.2.7 Training

All staff should be aware of the regulatory and statutory implications of the Authorisation for the process and their work activities.

Training should be given to all staff involved in process operation and this should include the environmental implications of their work and the procedures for dealing with incidents.

There should be records of the training given to staff.

### 3.2.8 Finance and accounting

There should be a good understanding of the costs associated with waste production within the process. This can be achieved by having accounting practices in place that ensure that waste disposal and other significant environmental costs are attributed to the processes involved and are not treated simply as a site overhead.

The process operator should be able to demonstrate that adequate resources are being committed to keep the process operating in compliance with the Authorisation.

## 3.3 Minimisation and abatement of releases to air

### 3.3.1 General

Hydrocarbon gases, unless required for further processing, should be put to constructive use where possible. This may include sale, use as fuel for gas turbines, heaters, furnaces, boilers, etc. Gas should be recovered and treated to remove sulphur. Where this is not practicable, any surplus should be flared, not vented.

Some organic compounds have low odour thresholds, and therefore the control of odours should be an integral part of the pollution abatement systems.

Activated carbon beds have been used to buffer organic loads being fed to treatment facilities such as biological filters. The bed adsorbs organic compounds during periods of high concentration and desorbs the pollutants during periods of low concentrations, thereby preventing the overloading of the biofilters. Adsorption is discussed further in Section (h).

Where possible, methods of determining the flowrates should be incorporated to aid control and quantification of releases.

Means for reducing, where appropriate, sulphur oxides, oxides of nitrogen and particulate matter should take into account techniques described in IPC Guidance Notes S2 1.01<sup>(a)</sup> for combustion processes and S2 5.01<sup>(a)</sup> for chemical incineration processes.

Means for dealing with polluting releases from pressure relief systems should be provided. Such means normally include phase separation where two-phase flow is possible, and may include venting to scrubber systems, to flare, to vent, or to an enclosed dump tank. Procedures should be in place to reduce to a minimum the likely frequency of such releases. It may be appropriate to have two relief devices in parallel set at different relief pressures. The lower set pressure can allow low release rates capable of being scrubbed in emergency equipment, whilst the higher set pressure deals with the low-probability high-flowrate event that cannot be abated and must be released at a sufficient height to promote dispersion and prevent hazardous concentrations at ground level or in buildings and plant structures. Processes must be operated in such a way as to protect the environment as well as persons at work.

Any credible abnormal events, including activation of emergency pressure relief devices, that could lead to release of materials to atmosphere should be identified on the application, giving the likely frequency of the event, quantities released, chemical species involved, their concentrations and discharge rates.

### 3.3.2 Releases of volatile organic compounds

The term "volatile organic compounds" includes all organic compounds released to air in the gas phase.

Where possible, the least environmentally harmful reactants and solvents should be chosen. There may be the opportunity to make a similar substitution in an existing process. The use of supercritical solvents may also be relevant.

#### (a) Minimisation at source of VOC emissions

The aim in all processes should be to prevent or minimise the release of VOCs. Because of the size, scope and nature of petrochemical and organic chemical works, this presents a major challenge requiring an overall strategy that also devolves down into individual action at process unit and plant item level. However, general principles may be noted.

In some processes, there may be a choice of feedstock. Feedstocks with a desirable specification will give a higher yield of the required product. They will also contain lower

quantities of impurities, such as sulphur, that might give rise to emission of inorganic pollutants. Purchase of a high-specification feedstock may shift the purification duty to the supplier. If the supplying plant is a large integrated facility, such as a refinery or petrochemical complex, it may be better suited to perform such purification. When it is feasible to consider different feedstock qualities, such as on a new plant, the issues may be more complex than a simple price differential. Supply and demand, and the close integration of petrochemical industry in general, will constrain the possibilities.

Catalyst design is important. A low yield per pass is not desirable, and requires substantial recycle. This has implications in cost and, typically, power use. More directly relevant is the selectivity. Low selectivity results in production of unwanted co-products that can be potential pollutants. Catalysts are specific to each process. The possibility of retrofitting an existing plant with a newer generation of catalyst should be considered where possible. Where the catalyst system is dispersed in the process medium, a highly active catalyst will require less 'ash' removal and associated treatment needs.

Where waste products or co-products also occur, emissions can be minimised by recovery and recycle. A purge of paraffinic hydrocarbons from a polyolefin plant recycle loop, for example, may be treated in several ways. One is to flare the purge or, preferably, to use as fuel. Ideally the purge can be recycled to join the feed to a cracker on an integrated site. The decision on whether to use as fuel or try to recover useful process streams is often complex, on environmental, regulatory and economic grounds. The possibility of recycling will be enhanced if streams of dissimilar composition are kept segregated. It should however be recognised that the use of by-product streams as fuel is integral to the economics and integration of many petrochemical processes.

Losses of VOCs may occur on occasions when equipment is opened. In some processes there is a regular need to open up, such as to descale reactors. Appropriate process design can minimise this need. For example, anti-caking chemicals may be sprayed automatically inside vessels. Cleaning systems may be designed with filter sprays so that the equipment does not need to be opened.

VOC material may be lost into cooling water or process water and then evaporate into the atmosphere. This can be minimised at the design stage by avoiding direct contact where possible between water and VOCs.

Direct contact with organic compounds occurs when:

- water is used to wash impurities from organic products from reactors, pipelines, etc;
- water is used to cool or quench organic vapour streams;
- steam ejectors are used to pull a vacuum on vessels containing organic compounds, and the steam is subsequently condensed;

- water is used as a carrier for catalysts and neutralising agents (eg caustic solution); and
- water is formed as a by-product from reactions.

Consideration should be given to pre-stripping of the waste water or use of an enclosed treatment method. Vented vapours should be passed to the fuel gas system, treatment plant or flare.

If the organic material is a main feedstock or product, there is usually a strong economic incentive to minimise inventory. It should also be noted that losses from tankage are influenced by throughput and movements of material as much as by the volume held. However, it is generally good practice to minimise holdings, particularly where the material is, for example, make-up to a recirculating solvent system.

### (b) Fugitive releases

Most VOCs are often released through fugitive losses from sources including valves, flanges, pump seals and equipment vents. The strategy and action priorities to be adopted by a works have necessarily to be developed by the operator in response to the demands of BATNEEC.

This Note cannot cover all the elements likely to be contained in such a programme. However, the principal areas of fugitive loss are well known and their minimising has been the subject of much investigation and action worldwide.

An essential first step of any programme is to establish a fugitive release inventory for the plant. This normally involves a combination of sampling, measurements, environmental monitoring, dispersion modelling and estimates based on emission factors. This is a major undertaking, which involves the following steps:

- Identifying all potential sources of VOC releases, by establishing population counts of equipment components in line with up-to-date piping and instrumentation drawings for processes. This survey should cover gas, vapour and light liquid duties.
- Quantifying of the VOC releases, initially as baseline estimates, and subsequently to more refined levels. Suitable protocols for this include the US EPA Method 21<sup>(33)</sup> for process component losses and API methods<sup>(34)</sup> for tankage losses. Some major companies have developed their own techniques and protocols.
- Using appropriate dispersion modelling techniques, predict atmospheric mass flux and concentrations.
- Employing environmental monitoring techniques (see Section 6), compare the predicted situation with the measured one.

Works should clearly tackle the largest losses first. In the case of process component fugitive releases the best available technique, probably the only real option, is the implementation

of a permanent on-going leak detection and repair (LDAR) programme. This should be developed and tailored to suit the situation concerned, using appropriate techniques, frequencies and priorities. It should provide estimates of fugitive VOC releases for monitoring returns and enable action to be taken to minimise releases.

LDAR programmes have been used successfully worldwide to reduce VOC releases and are already in use in the UK. Typical survey results show that leaks from glands on valves and pumps are responsible for 90% or more of estimated fugitive releases and that a small proportion of valves, virtually all on gas or high-temperature light material streams, contribute almost all of the total. Abatement of fugitive releases is of particular importance for VOCs with a high environmental impact (Category A). Best available techniques used to minimise such process component fugitive releases include the following:

- Use of low-emission valve stem packing (500ppm) on critical valves, eg rising-stem gate-type control valves in continuous operation, particularly on gas/light liquid high-pressure/temperature duties.
- Use of alternative proven types of low-release valves where gate valves are not essential, eg quarter-turn and sleeved plug valves, both of which have two independent seals.
- Use of balanced bellows-type relief valves to minimise valve leakage outside of design lift range and piping of reliefs to flare, normally via phase separation, without header back-pressure.
- Minimising the number of flanged connections on pipelines and the use of high-specification jointing materials.
- Use of canned pumps, magnetically driven pumps, or double seals on conventional pumps.
- Piping of compressor seals, vent and purge lines to flare systems.
- Use of end caps or plugs on open-ended lines and closed loop flush on liquid sampling points.
- Minimising the releases to air from process hydrocarbon analysers, by optimising sampling volume/frequency and venting to flare systems.

### (c) Storage and transfer

Raw materials, intermediates and products with a true vapour pressure (TVP) of 14 kPa or above at maximum run-down temperature, or odorous substances, should be stored so as to minimise releases to air. Techniques available include floating roof tanks with primary and secondary seals, fixed roof tanks with internal floating covers and rim seals, fixed roof tanks (with or without gas blankets) venting to suitable arrestment plant, or pressure storage. Suitable arrestment techniques are



combustion, condensation, absorption and adsorption. If combustion is chosen then the installation of flame arresters or other detonation safeguards is necessary. In general bulk storage temperatures should be as low as practicable and temperature changes due to, eg, solar heating, should be taken into account. Techniques to minimise storage temperature include cooling of the tank inlet stream, insulation of the tank, and painting the surface white.

The loading and unloading of transport containers, or transferring material from one vessel to another, should be carried out so as to minimise the release of pollutants to air. Techniques available include subsurface filling via filling pipes extended to the bottom of the container, the use of vapour balance lines that transfer the vapour from the container being filled to the one being emptied, or an enclosed system with extraction to suitable arrestment plant.

When filling ships, rail cars or road tankers with some form of loading arm, these should be fitted with sensing devices for detecting undue movement, and pressure/vacuum sensors for detecting accidental spillage and leakage. Self-sealing hose connections are also good practice.

Techniques to prevent overfilling of storage tanks include level measurement, independent high-level alarms, high-level cut-off, and batch metering.

#### (d) Miscellaneous

Releases to air from process and cooling water systems and associated treatment plant should be minimised. Techniques include ensuring that initial contamination is minimised by provision of adequate phase separation facilities, that any intermediate stripping is efficient and enclosed drainage to treatment plant (separators, etc) is used.

The aim should be to prevent organic and particulate matter releases to air during plant cleaning, equipment decoking, catalyst regeneration, catalyst discharging and charging operations, and catalyst and sludge disposal. Techniques available include venting and steaming vessels to flare, discharge of vessel contents to enclosed vessels with suitable treatment, eg filters and drum storage.

Where appropriate, heating or cooling circuits should be monitored for process fluid contamination. Temperature alarms should be fitted to warn of overheating/cooling.

Lagging should be fitted where this would minimise energy usage, material degradation and fluctuations in temperature. Trace heating with some form of thermal cut-off protection should be installed where there are risks of solidification and resultant damage to plant.

Vent systems should be chosen to minimise breathing releases, eg pressure/vacuum valves, and, where relevant, should be fitted with knock-out pots and appropriate abatement equipment.

Suitable barriers should be provided to prevent damage to equipment from the movement of vehicles.

#### (e) Controllable emissions

Vapour recovery is the preferred BAT for the abatement of VOC releases where it is practicable to capture them and where possible they should be returned for process or fuel use. Available techniques are described in HMIP Technical Guidance Note A2<sup>(19)</sup>, and include the following:

- condensation;
- absorption;
- adsorption;
- biofiltration and bioscrubbing; and
- thermal decomposition.

This is not an exhaustive list of acceptable techniques and as other systems are developed they should be evaluated for individual processes. See also ETBPP guides <sup>(20)</sup>

#### (f) Condensation

Potentially, condensation is the simplest technique for recycling substances and minimising waste. Where appropriate condensation should receive strong consideration as the primary abatement technique, for example upstream of plant scrubbers.

Condensation is generally achieved by indirect heat exchange, eg in a shell-and-tube heat exchanger, with cooling water, possibly chilled. Coolant temperature should be justified with reference to the vapour quantity discharged. Some systems operate down to -75°C using a series of refrigerated condensers with progressively lower temperatures to prevent process blockage. The use of scraped heat exchangers should also be considered.

Where liquid nitrogen is used as a source of blanket gas, its evaporation can provide integrated refrigeration to cryogenic temperatures.

Monitoring of cooling fluid temperature and flow are required to assess the efficiency of the condenser. A low-flow alarm and coolant high-temperature or exit vapour stream high temperature alarm, or equivalent, should be required to register upset conditions likely to affect the performance of the condenser.

For the specific case of a reflux condenser on a batch reactor, the cooling capacity of the condenser should, where possible, be in excess of the heating capacity of the reactor, as well as being capable of achieving the desired vent temperature.

#### (g) Absorption

##### General

The absorbent or scrubber liquor can be water, caustic, acidic or other neutralising substance or oxidising reagent according

to the nature of the contaminants to be removed. The absorbent may be recycled round the absorber or passed to a recovery system.

To achieve optimum transfer from the gas phase to the liquid phase it is important that:

- maximum interfacial contact between gas and liquid phases is maintained;
- sufficient residence or contact time for absorption is allowed; and
- the contaminant is readily soluble in the absorbent.

In most cases the absorbent flows counter-currently to the exhaust gas so that the most dilute gas is contacted with the most pure absorbing liquor, providing a maximised concentration difference for the entire length of the column. This arrangement results in the highest theoretical removal efficiency.

A standard process for recovering solvents from waste air streams uses a combination of: absorption to absorb the vapours into a liquid stream; distillation or degassing to separate the resulting mixture into its individual components; and condensation to recover the solvents in a usable form. The scrubbing liquid is chosen according to the type and solubility of the organic contaminants.

It should be noted that wet collection devices can be used for these purposes as well as for particulate matter control.

Absorption of solvents into oil is a very effective recovery method for those solvents possessing lipophilic properties, especially halogenated organic solvents such as dichloromethane.

Consideration should be given to using an absorbent that can be used directly in the same process, for example by using an appropriate raw material or solvent as the absorbent to recover solvent or partially reacted products such that they can be recycled to the process, or used elsewhere.

Instrumentation and alarms should be installed to ensure that liquid level and flowrate are maintained and that the pressure drop remains constant. Low-temperature alarms may be necessary to warn of freezing. Concentration of absorbent should also be monitored. Scrubbers should include sample points upstream and downstream to allow analysis of inflow and outflow gas concentrations.

### *Packed and plate tower scrubbers*

In a packed tower scrubber the packing material provides a large surface area for mass transfer between liquid and gas phases. In the plate column the plate disperses the gas into numerous bubbles, so creating a large surface area for mass transfer.

The even distribution of scrubbing liquor and prevention of plugging or channel flow is of critical importance to the satisfactory operation of such a system.

The advantages of packed tower scrubbers include generally modest to low pressure drops, and ease of construction with chemically resistant material.

Packed tower scrubbers are generally best suited to situations where a high gas removal efficiency is required and the exhaust gas to be treated is relatively particulate-free. Plate column scrubbers are more effective for dealing with gas streams containing particulate material and can more readily accommodate fluctuations in flowrate and temperature. Fluidised-bed packed towers are particularly effective at overcoming solids blockage problems.

Where a scrubber is used for odour control the absorbent is often an oxidising reagent such as potassium permanganate or sodium hypochlorite.

### *Spray towers*

Spray towers can achieve good removal rates for readily absorbable contaminants. Mass transfer is achieved by atomising the absorbent using nozzles and may be enhanced by the use of appropriate surfactants.

The simple design allows relatively easy construction in corrosion-resistant material and ease of maintenance.

The advantages of these units include cheapness and minimal energy requirements due to low pressure drop. However, regular checks should be made to ensure that the nozzles are neither excessively worn nor clogged, particularly if the gaseous stream contains particulates. Where appropriate, pressure gauges should be installed.

Specialist spray scrubber designs, using high-pressure liquor, can treat gases to plate tower standards without fouling or solid blockage problems.

### *Wet mop scrubbers and rotacloones*

In wet mop scrubbers, absorbent is injected into the impeller casing where it is atomised and mixed with an extracted air stream. The impeller is usually of an absorbent and flexible fibrous material. The exhaust stream is demisted and the absorbent either discharged to drain or recirculated to the impeller casing via a holding tank.

Rotacloones operate in a similar manner to wet mop scrubbers except that the impeller is rigid. Rotacloones tend to be used for higher flowrates, wet mop scrubbers for lower ones.

### **(h) Adsorption**

Adsorption describes the removal of gaseous components from a gas stream by adherence to the surface of a solid. The gas molecules removed are referred to as the adsorbate and the

solid to which the molecules adhere is the adsorbent. Adsorbents are highly porous materials.

Adsorption is used for air purification and solvent recovery. The most common adsorbents are activated carbon, silica gel, activated alumina and zeolites.

The polarity of the surface of the adsorbent determines the type of vapours for which the adsorbent has the greatest affinity.

Polar adsorbents will preferentially adsorb any water vapour present in the gas stream. Since moisture is present in most gaseous waste streams from the organic chemical industry, their application to pollutant removal is limited.

Activated carbon is the only common non-polar adsorbent. It is used to control releases of organic solvents, odours, toxic gases, acid vapours, phenols and hydrocarbon vapours.

Adsorption is an exothermic process; therefore, carbon adsorption may not be an appropriate technique for highly concentrated streams of organic compounds with high heats of adsorption. The molecular weights of the compounds to be adsorbed are generally in the range of 45-130. Properly operated adsorption systems can be very effective for homogeneous off-gas streams, but may be unsuitable for a multicomponent system containing a mixture of light and heavy organics. The presence of water can severely reduce reclamation efficiency. The lighter organics tend to be displaced by the heavier (higher-boiling) components, reducing system efficiency.

#### *Activated carbon adsorption*

Activated carbon beds can generally be used within the processes covered by this Note to control releases from storage tanks and can often be used as a polishing treatment after condensers and scrubbers.

Carbon adsorption systems usually take the form of multiple-bed systems, with one on-line, one regenerating and one on stand-by. The contaminated gas stream should be pre-treated to remove any particulate matter or entrained liquids. The gas stream is then passed down through the fixed carbon bed. Upward flow through the bed is usually avoided because of the risk of entraining carbon particles in the exhaust gas.

As the temperature increases, the capacity of an adsorbent decreases since the energy level of the adsorbed molecules increases. This gives them sufficient energy to overcome the van der Waals attraction and migrate back to the gas phase.

As a general rule adsorbents operate below 55°C. Any increase in pressure will increase the adsorption capacity of a system.

The residence time in the adsorber is dependent on the gas velocity (the slower the gas passes through an adsorber, the greater the probability of a contaminant molecule hitting an available site) and the size of the adsorber unit. Consequently,

providing sufficient bed depth and low gas velocity are important design factors.

High humidity can interfere with the adsorption process. Similarly, other entrained compounds and particulate matter interfere with the adsorption of gas molecules. The humidity levels, temperature and pressure during the adsorption should be monitored to maintain optimum efficiency.

Inspectors should ensure that it is possible to measure the performance of any adsorption equipment, ie sample points should be in place to facilitate the analysis of inflow and outflow gas streams. The adsorption equipment should be monitored for breakthrough. Similarly, other parameters such as temperature and pressure should be monitored.

Hot spots when adsorbing, eg, ketones can be controlled with water quenching.

#### *Regeneration*

Periodic regeneration of the adsorbent bed is required to maintain removal efficiencies. The organic material recovered from the bed should preferably be re-used.

Inspectors should ensure that adequate provision for regeneration is available and that an ultimate disposal route for the adsorbent has been identified.

Regeneration can be achieved by several techniques. A few in situ methods are described below. Further details are available in IPC Guidance Note S2 5.03<sup>(1)</sup>, Cleaning and Regeneration of Carbon.

Eventually, carbon loses its ability to be regenerated in situ, because of residual organic compounds, and is disposed of as waste or preferably returned to the supplier or a third party for regeneration.

An option for regenerating carbon beds that eliminates waste water associated with steam is to pass hot combustion air for an incinerator through the carbon bed. The desorbed organics are carried in a concentrated stream to the incinerator and burned as fuel, decreasing or eliminating the need for auxiliary fuel. However, it should be remembered that re-use of the adsorbate is the preferred option.

#### *Thermal swing (steam stripping)*

The bed is heated to lower the adsorption capacity. Thermal swing represents a simple and relatively inexpensive desorption technique. At steam pressures of between 1 and 3 barg the temperature of saturated steam is sufficient to desorb most solvents without damaging the adsorbent. The resultant waste stream from the steam stripping can be separated by condensation, distillation or by phase separation techniques.

Steam stripping is the most widely used desorption technique in industry.

The disadvantages of this technique include: the production of an aqueous waste stream requiring treatment; steam stripping of contaminants that may hydrolyse can cause the formation of corrosive solutions that may damage the adsorption equipment; cooling and drying of the bed may be required after steam stripping to ensure the renewal of adequate removal efficiencies.

### *Pressure swing*

Pressure is reduced to lower the adsorbent capacity of the beds. Desorption is achieved by a change in pressure rather than temperature and no time is lost in heating or cooling the beds. An aqueous waste stream is not generated by this method. The principal disadvantages include the high operating and initial construction costs.

### *Displacement of adsorbate*

The adsorbate can be desorbed by the introduction of a preferentially adsorbed material that will release the pollutants.

The desorbed adsorbate may require further treatment prior to recycle or discharge to the environment.

## **(i) Biofiltration and bioscrubbing**

Biofiltration represents a relatively new biological treatment method for gaseous waste streams. It generally uses beds of peat/heather or other organic materials, eg bark or some composts. Bioscrubbing on the other hand takes place in towers containing a bioflora.

In biofiltration, waste gases pass through a filter reactor in which micro-organisms are fixed in a water phase within the filter material. The water content within the filter is critical to its effectiveness and, since the gas flow through the reactor will tend to evaporate it, a humidification stage is often included upstream of the biofilter.

Hot gases may need to be cooled closer to the optimal activity temperature for aerobic micro-organisms, generally 25 to 35°C. The potential temperature rise across the bed of up to 20°C should be taken into account.

Biofiltration and bioscrubbing have lower operating costs than many other air pollution control technologies for treating low concentrations of biodegradable organic pollutants. They are used in particular for the abatement of odorous emissions. Bioscrubbers have the higher maintenance cost of the two. Environmental benefits include low energy requirements and the avoidance of cross-media transfer of pollutants.

The major operating parameters such as the off-gas temperature and back-pressure should be checked daily. Similarly the moisture content in the filters should be monitored regularly. A low-temperature alarm should be fitted to warn of freezing, which may damage the filter and may affect the growth of the microbial population.

Consideration should be given to the effect of loss of biomass

due to the introduction of toxic compounds and a stand-by procedure should be developed for such an event.

## **(j) Decomposition**

Thermal or catalytic decomposition processes should be considered for non-biodegradable, toxic pollutants in the gas phase where further recovery cannot be achieved.

Four basic decomposition processes can be employed: thermal incinerators, catalytic incinerators, flares and process boilers. The applicant should justify the choice of process.

On all types of thermal decomposition equipment, sampling points should be in place for monitoring the performance of the combustion process. Several parameters should be continuously monitored. These should include flame failure, which should trigger an alarm, the combustion temperature and pressure.

### *Thermal incineration*

Thermal incinerators are used to control waste gases containing low concentration of organic vapour.

The temperature of the incinerator and the gas residence time are the most important operational variables. The calorific value of constituents in waste streams also varies and a supplementary fuel may be required. Heat recovery is important in minimising fuel use and cost. Recuperative or regenerative systems are widely used. Reference should be made to the Waste Incineration Guidance Note IPCGN S2 5.01<sup>(32)</sup> for achievable release levels.

### *Catalytic oxidisers*

The inclusion of a catalyst in an incineration process allows the oxidation reaction to take place at a lower temperature and at a faster rate than in a thermal incinerator. However, catalytic oxidisers tend to be less robust: waste streams containing particulate matter cannot be destroyed effectively in a catalytic incinerator since particles may blind the surface of the catalyst. Similarly, catalytic oxidisers can be affected by waste gas constituents, eg acetic and acrylic acids or poisoned by sulphur compounds.

All catalysts deteriorate with use and need to be replaced periodically. A safe disposal route for the catalysts should be identified. In many cases the catalysts are returned to the manufacturer for regeneration.

The performance of the catalyst should be monitored regularly so that any deterioration is noted at an early stage and remedial action taken.

### *Flameless thermal oxidisers*

These allow oxidation at reduced temperature by passing the waste gas through a preheated ceramic packing. In the absence of a flame, formation of NO<sub>x</sub> is reduced. A similar effect may be achieved in a regenerative system operating under autothermal conditions.

## Flares

Direct combustion or flaring can be used for the destruction of intermittent or emergency emissions of combustible gases. Whilst there is no suitable alternative to a flare system for dealing with emergency releases, deliberate continuous flaring of process vents should be discouraged as there is insufficient control over the combustion exhaust gases.

The flare system should be carefully designed to allow combustion of all gases necessarily vented to it under all circumstances. The basis of the worst case should be justified. The effect of low gas flow and wind dilution should be considered and allowed for in the design. Flares should burn without smoke under all conditions and should be designed to accommodate varying flowrates.

The applicant should justify flare heights.

Knock-out pots/drums should be installed as close as practicable to the flare to catch liquids and condensable material.

Problems associated with flare systems include:

- the heat generated may be unacceptable without careful design;
- the light/luminescence of the flame may be a nuisance if the plant is near an urban settlement, and concealed combustion chambers/ground flares should be considered in such cases;
- flare tip mixing systems can cause increased noise levels;
- incomplete combustion of organic compounds;
- both oxygen starvation and oxygenated flames can give rise to emissions of toxic or obnoxious substances;
- the flaring of halogenated substances should be avoided;
- flares need to be kept lit constantly with robust pilot light and flame failure alarms should be installed on pilot lights;
- heat cannot be recovered;
- constant purging is generally required; and monitoring of releases from flares is generally impracticable, making it difficult to ensure adequate combustion.

Flare gas recovery systems should be considered to minimise flaring.

Further information on flares is available in Technical Guidance Note A1<sup>(10)</sup>.

### 3.3.3 Particulate matter

The methods available for minimising or reducing discharges of particulate matter to the atmosphere include:

- cyclones;
- fabric filters;
- ceramic filters;
- wet collection devices;
- electrostatic precipitators both wet and dry; and
- dust suppression equipment.

The appropriate technique depends on the characteristics of the particles and the carrier gas stream, process factors such as temperature and pressure, and operational factors including structural limitations such as floor space and head room.

Further information is available in Technical Guidance Note A3<sup>(10)</sup>.

There is little scope for the use of electrostatic precipitation in the organic chemical industry; this gas cleaning technique is inappropriate to risks of fire and explosions where used in systems handling flammable organic materials. Consequently, the application of electrostatic precipitators is not discussed further.

#### (a) Cyclones

Cyclones are the principal type of gas solids separator employing centrifugal force, and are widely used. They can be manufactured from a wide range of materials; and can be designed for high-temperature and pressure operation. Cyclones are suitable for separating particles down to about 5µm; smaller particles down to about 0.5µm can be separated where agglomeration occurs. High-efficiency cyclones are capable of removal efficiencies of the order of 90% for particles down to 5µm. At smaller particle sizes the collection efficiency drops off appreciably. High-gas-rate cyclones have a removal efficiency of about 90% for particle sizes down to about 20µm. The most commonly used design is the reverse flow cyclone, where gas enters the top chamber tangentially and spirals down to the apex of the conical section. It then moves upward in a second, smaller-diameter, spiral and exits at the top through a central vertical pipe. Gas pressure drops tend to be of the order of 10-70 mm water gauge.

#### (b) Fabric filters

The industrial fabric filter is generally constructed from a woven material or a felted fabric to provide the filtration medium through which the particle-laden gases are passed.

Fabric filters are particularly useful as secondary or tertiary gas cleaning devices with a cyclone, dry scrubber or fluidised-bed absorber located upstream.

Filter efficiency may be enhanced by pre-coating the filter cloth prior to being brought on-line.

Fabric filters are not generally suitable for use in moisture-laden streams or those with acidic, tarry or sticky characteristics due to the adverse effects of fabric 'blinding' and adherence problems.

Regular maintenance and cleaning of the filters is necessary to maintain removal efficiencies.

The performance of the fabric filters may be monitored by measuring the dust concentrations upstream of the filters and in the exhausted gas stream. Bag failure should be alarmed using, say, an opacity meter, or particle impingement detector or by appropriate pressure drop monitoring.

### (c) Ceramic filters

Ceramic filters are constructed in two varieties: high-density and low-density. The high-density unit comprises a silicon carbide base with a fine coating (usually aluminium silicate). The low-density unit comprises a matted mixture of silica and alumina fibres.

The high-density units generate a higher pressure drop than the lower density type.

They are both capable of withstanding temperatures up to 900°C and instantaneous temperature shock from 900°C to 0°C.

Filtration efficiencies greater than 99.9% for particulates down to sub-micrometre sizes are attainable.

Regeneration is achieved by reverse air pulse at about 7 barg, an operation similar to that undertaken with bag filters.

### (d) Wet collection devices

Wet collection devices use a variety of methods to wet the particles to remove them from a gas stream. The technology available varies in terms of cost, collection efficiency and energy requirements. Increased energy results in increased collection efficiency for particulate matter. They include venturi, jet, dynamic, centrifugal and impingement scrubbers but generally only the first two are suitable for sub-micrometre particles.

Wet collectors have a constant pressure drop and do not present secondary dust problems. However the design should ensure that mists and fumes cannot be formed. They can handle high-temperature gas streams and moisture-laden gas streams. They can also handle corrosive gases and aerosols.

In a venturi scrubber the gases are drawn into the throat of a venturi tube to which pressurised water is injected. There are two basic types: low and high-pressure drop. Pressure drops at the lower end of the range (250 mm water gauge) are generally adequate for the removal of particles of a few micrometres in diameter.

For sub-micrometre particles the upper range of the pressure drops (1500 mm water gauge) may be required particularly if better than 99% collection efficiencies are required.

The performance of scrubbers should be measured by analysis of the exhausted gas and of the scrubber liquor. The pressure drop across the scrubber and the level of scrubber liquor should also be monitored.

### (e) Dust suppression equipment

Wherever possible raw materials should be contained in silos, storage tanks, or covered areas. The storage of dusty materials by stockpiling requires some form of dust suppression. Continual maintenance of a sufficient moisture level on the surface of stockpiled dusty material may be necessary to arrest dust pollution.

#### 3.3.4 Cooling towers

Several types of cooling tower are in common use. These include:

- ☐ air cooling;
- ☐ natural draught cooling towers; and
- ☐ low-level mechanically assisted cooling towers.

Condensed plumes that come down to ground level can bring droplets containing biocides, or organisms that could be harmful, and can also cause loss of light, poor visibility and icing of roads. Such plumes should not be permitted.

Where plumes need to be abated the temperature and the humidity need to be controlled. This may be achieved by combining conductive heat exchange and evaporative cooling in the design of the cooling tower. The degree of abatement required will depend upon local conditions and the distance from the towers to the nearest sensitive area. Plume modelling should be employed by the operator to confirm that the visible (condensed) plume will not ground beyond the boundary fence nor reach areas of habitation at a height that will cause significant loss of light. (As a guide the width of the plume should not fill an arc that subtends an angle greater than 10° when viewed vertically upwards from the ground.)

An operator may propose to guarantee to reduce load or to take other appropriate action to ensure that the above conditions are met. Performance curves should be provided to enable the plume abatement to be demonstrated under a wide range of ambient conditions.

#### 3.3.5 Vent plumes

Releases from vents generally should be hot enough to avoid visible plume formation in the vicinity of the vent. This is to prevent the condensation or absorption of environmentally harmful substances by the condensing water vapour. Exhaust gases from a wet scrubber can be heated by the use of waste process heat to raise the exit temperature of the exhaust gases and prevent immediate condensation on exit from the vent. This procedure also assists the thermal buoyancy of the plume. Where there is no available waste heat and the vent contains no significant environmentally harmful substances, the applicant may be able to demonstrate that the BATNEEC/BPEO criteria have nonetheless been met.

#### 3.3.6 Refrigeration systems

Best available techniques are to avoid the use of refrigerants of significant environmental concern that will escape during

operation. New and replacement plants should not use chlorofluorocarbons (CFCs) or similar materials, eg hydrochlorofluorocarbons (HCFCs). The use of hydrocarbons, eg propane or butane, is considered the best available technique. Refrigeration systems should be subject to LDAR programmes.

### 3.3.7 Dispersion from chimneys and vents

The applicant will need to demonstrate that an appropriate assessment of vent and chimney heights has been made to provide adequate dispersion of prescribed substances, and other substances that might cause harm, which cannot be prevented - and may be released. Some guidance is given in Technical Guidance Note D1<sup>(4)</sup>.

For all major sites it is considered BAT for dispersion modelling to be carried out which takes into account local meteorological data, local structures and topography, as well as other local releases to provide estimates of process contribution to ground-level concentrations of significant pollutants at appropriate production and ambient scenarios. Inspectors should expect operators (or relevant experts acting for them) to produce and maintain an up-to-date multi-stack dispersion model for the works. Operators should provide clear information on the parameters used and the assumptions made in their use of dispersion models. Of particular relevance will be the assessment of background concentrations of pollutants and the fate in the environment of pollutants released. Statutory air quality standards<sup>(10,11)</sup> and other recognised criteria relating to international obligations should be taken into account. When a significant change is being considered which could lead to an Authorisation variation, eg new plant, uprated existing plant or major feedstock quality change (outside the normal range), the Inspector should require a new dispersion model to be presented. This should take into account the proposed changes and show the environmental impact of making them.

Where appropriate the operator should also recognise the chimney or vent as an emergency release point. Process upsets or equipment failure giving rise to abnormally high release levels over short periods should be assessed. Even if a very low probability of occurrence can be demonstrated by the applicant, a value for the chimney or vent height should nevertheless be set to avoid any serious damage to health.

The assessments made by the operator should be validated using the appropriate calculations or dispersion models available to the Agency:

All releases must be controlled and minimised to ensure that ambient air quality beyond the process boundary complies, as a minimum, with air quality standards<sup>(4)</sup>.

### 3.3.8 Odours

Substances present in emissions to air, which are known to be odorous, should be identified and quantified. Techniques described in this Note should be employed to ensure that they are minimised to prevent them being noticeable outside the site boundary.

## 3.4 Minimisation and treatment of releases to water

### 3.4.1 General

Waste water can arise from the process, from storm water, from cooling water, from accidental releases of raw materials, products or waste materials and from fire-fighting. These should all be taken into account when dealing with the process Authorisation.

It is very common for the aqueous effluents from several process plants to be treated together, in a site waste-water treatment system or as a combined stream to external treatment. Waste-water treatment is therefore often outside the scope of the process Authorisation. It must be recognised that synergistic effects may occur when effluents are mixed. Acids and alkalis may neutralise each other, for example. A dilution effect may be acceptable if it permits a pollutant to be destroyed in a biological system. However, the dilution effect alone should not be used to achieve permissible final effluent quality. Treatment at the process plant may be required.

The following techniques should be considered for reducing waste-water discharges:

- Minimise the presence of water in the process including water used in or produced as a by-product of reactions, product purification and equipment cleaning.
- Recycle waste-water back to the process or to secondary uses such as equipment wash-down, using water pinch analysis if applicable<sup>(25)</sup>.
- Employ indirect contact heat exchange devices.
- Segregate process water, storm water, and indirect cooling water streams to reduce the hydraulic loading to waste-water treatment equipment or sewers.
- Develop spill contingency procedures to minimise the risk of accidental release of raw materials, products and waste materials and to prevent their entry into water.
- Where possible, roof bunded areas to minimise the volume of potentially contaminated storm water.
- Use dry cleaning methods wherever practicable for solids. Vacuum extraction reduces the loss of product to the waste-water and, in some cases, allows the recovery of these products.
- Wipe down equipment that is accessible, rather than washing and rinsing it.

The characteristics of releases to water from a plant largely depend upon the type of process involved, the standards of housekeeping, the degree of recycling achieved and whether or not potential releases to air are transferred into the aqueous media, eg by gas scrubbing.

Aqueous wastes may contain a wide range of organic compounds as well as particulate matter. The effluents produced by the processes covered in this Note may need to be neutralised.

The neutralisation of an acid waste with an alkaline waste should be considered if compatible streams are available. However, care should be taken to avoid discharging alkaline solutions, contaminated with sulphur compounds, into low-pH waters, because there is a risk of subsequent release of those compounds in gaseous form.

Where appropriate, liquid effluents of different characteristics should be segregated for treatment by the most appropriate methods.

Treatment chemicals such as corrosion inhibitors, descaling agents, sodium hydroxide and biocides should be chosen such that they minimise substances prescribed for water, eg use of mercury-free sodium hydroxide. They should be stored in sealable bunded areas, or equivalent, and returned to those areas after use.

Storage tanks and process vessels should be bunded. The bunding arrangements should be subject to risk assessment and be capable of containing at least 110% of the capacity of the largest tank within any one bund. Bunds should be impermeable and should have no direct connection to drains. Bunds not frequently visited should be fitted with a high-level probe and an alarm as appropriate.

Bunds should be regularly inspected for structural integrity by a competent person. The Environment Agency has issued guidance on tank storage<sup>(39)</sup>.

Separated organic chemicals should be skimmed off in a manner that prevents air pollution and, where practicable, should be recycled to the process.

A site-specific spillage contingency plan should be prepared and suitable materials and equipment held on site.

Process waters, site drainage waters and chemically contaminated waters should where appropriate be treated, primarily to remove organic compounds.

### 3.4.2 Water collection

#### (a) Process waters

Process waters are those obtained as a result of the processes carried on in the chemical works and arise from specific plant items. Examples include: tank bottom drainings; distillation condensates; purge streams; blow-down waters; and drainage from process, handling and storage areas.

As a consequence of their direct contact with other process fluids, process waters may have absorbed organic compounds and may be emulsified. Accordingly, they should be conveyed from source via an appropriate sewer to treatment plants in a closed system as far as practicable.

The quantity and nature of contamination will be largely site-specific but can generally be categorised as:

- waste-water streams contaminated with hydrocarbons;
- waste-water streams contaminated with chlorinated hydrocarbons; and
- acidic and alkaline waste-water streams.

Waste waters containing chlorinated hydrocarbons should where possible be treated separately to ensure proper control and treatment of the chlorinated compounds. Released volatile chlorinated hydrocarbons should be contained and vented to suitably designed incineration equipment.

Potential releases from vacuum systems should be minimised by the following methods:

- Vacuum lines should pass through knock-out pots and separators for recycle wherever possible.
- The use of process fluids for liquid ring pump sealing should be considered together with the subsequent use of these contaminated streams within the process.
- Consideration should be given to the use of dry vacuum pumps, which do not use either a sealing fluid or lubricating oil.
- Where sealing fluids are used, the installation of closed systems should be considered together with heat-exchange equipment and scrubbing facilities where required.

#### (b) Site drainage waters

These are essentially rain water running off hard surfaced process areas or collected by purpose-designed drains.

They may be contaminated with organics but are not generally emulsified. Accordingly, they should be passed to a treatment plant, via an oil separator<sup>(40)</sup>.

Stocks of suitable absorbents should be held at appropriate locations for use in mopping up minor leaks and spills, and should be disposed of to leak-proof containers.

The site drainage should be designed such that spillages of chemicals, lubricants, etc, should be routed to the effluent system, with provision to contain surges and storm-water flows<sup>(41)</sup>.

The collection system should also take account of the additional fire water flows (BS 5908<sup>(42)</sup> gives some guidance), or fire-fighting foams. Emergency storage lagoons may be needed to prevent contaminated fire water reaching controlled waters.

#### (c) Cooling waters

Discharges from once-through cooling water systems or other sources should not be used to achieve, by dilution, release



limits for substances prescribed for water being discharged from treatment plants.

Cooling waters are generally used in indirect, recirculatory systems.

### 3.4.3 Treatment methods

Further information is available in Technical Guidance Note A4<sup>(4)</sup> and ETBPP guides <sup>(5)</sup>.

#### (a) Introduction

It is unlikely that any single waste water treatment technique will be adequate to render harmless the waste water to be discharged. For example, a waste water stream with a low pH and a high organics content would require both pH adjustment and a means for rendering harmless the organic compounds.

Treatment methods including combinations of those below should be applied as appropriate.

#### *In-plant treatment*

- For heavy metals, combinations of: oxidation/reduction; precipitation; filtration.
- For organics, combinations of: oxidation; air or steam stripping; granular activated carbon; wet oxidation; ion exchange; reverse osmosis; electrodialysis.

#### *Primary treatment*

Primary treatment prepares the waste waters for biological treatment. Large solids are removed by screening, and grit is allowed to settle out.

- Neutralisation
- Coagulation/flocculation
- Flotation/sedimentation

#### *Biological roughing*

- Trickling filter
- Anaerobic-treatment

#### *Secondary treatment*

This is the biological degradation of soluble organic compounds typically from 50-1000 mg/l Biological oxygen demand (BOD)<sub>5</sub> to under 15 mg/l.

- Aerated lagoon
- Rotating biological contactors

- Activated sludge

#### *Tertiary treatment*

- Filtration
- Ozonation
- Granular activated carbon (GAC) adsorption
- Powdered activated carbon
- Nitrification/denitrification

#### *Sludge dewatering*

Waste solids in slurry form are produced by primary sedimentation, secondary clarification, and various in-plant treatments and pre-treatments. These sludges typically have to be thickened and dewatered before they can be landfilled, incinerated or otherwise disposed of. Methods available include combinations of:

- Gravity thickening
- Dissolved-air flotation
- Filtration
- Drying
- Centrifugation
- Sludge digestion

#### *Sludge Disposal*

Depending on the nature of the remaining sludge this can be disposed of to:

- Land
- Lagoon
- Incinerator
- Encapsulation

The following sections describe techniques available for treating the various contaminants.

#### (b) Immiscible organic chemicals/water separation

Techniques for separating immiscible organic chemicals and water streams, which could then be treated separately, include:

- American Petroleum Institute (API) separators;
- tilted plate separators;

- electrostatic coalescers;
- dissolved and induced air flotation;
- hydrocyclones;
- use of acceptable physical coalescing agents;
- ultrafiltration; and
- surface-modified cellulose filters.

### (c) Stripping sulphur contaminants

Removal of sulphur contaminants can be achieved by steam or air stripping. If the concentrations are low an acclimatised biological treatment system may be more appropriate.

This process is especially useful for process water contaminated with hydrogen sulphide, carbon disulphide, carbonyl sulphide or low-molecular-weight mercaptans.

Contaminated effluent is pumped to the top of the stripper, which can be either a packed tower or a plate column. Steam is injected into the bottom of the tower or, alternatively, the tower may be fitted with a steam-heated reboiler. Overheads are condensed and the condensate is returned as reflux to the column. The sulphide- or mercaptan-rich gas passes to a sulphur recovery unit or to incineration.

The potential releases can be minimised by the following methods:

- Vents from the feed vessels should be directed to the contaminated vapour treatment system.
- The steam stripper is of critical importance in maintaining final effluent quality and preventing odour problems. Therefore, standby stripping facilities should be provided or valid alternative methods of treatment should be available.

Care should be taken when selecting construction materials, particularly for the column overhead equipment, since severe corrosion can be encountered. Contaminated effluent steam strippers are prone to plugging and sequestering agents are frequently used to prevent calcium deposition.

The potential releases into water arise from inadequate stripping performance.

Sludges will be generated by separation of fines from effluent streams.

Solid wastes containing potentially acidic materials should be neutralised prior to disposal to landfill. Such wastes can be mixed with dry lime.

The remaining vapour stream may well require further treatment or recovery.

### *Volatile organic compounds*

Steam or air stripping can also be used to remove volatile organic compounds from the effluent stream. This will reduce subsequent desorption to atmosphere as well as decreasing the concentration in the effluent. The stripped VOCs require appropriate recovery or destruction. One option is to return air laden with VOC to a boiler or fired heater, provided that combustion conditions are appropriate. For chlorinated organic compounds, recovery is preferred or, if essential, combustion at hazardous waste incinerator conditions.

### (d) Neutralisation

Acidic or alkaline effluents should be dosed with an appropriate neutralising agent to achieve the required pH for the receiving water. pH control should be carried out in a vessel constructed of suitably resistant material. The vessel should be designed to allow a suitable retention time for dosing and mixing.

Where large discharges of effluent with high or low pH are possible, consideration should be given to a two- or three-stage feed-forward pH control system.

Care should be exercised with acid dosing effluent containing soluble toxic gases. The vent from these vessels should pass to scrubbing facilities.

Dosing systems are unable to cope with effluents of extreme pH; therefore, an intermediate facility capable of storing strongly acidic or alkaline effluents should be installed with automatic control if such effluents are likely.

The control of pH is difficult since the relationship between pH and concentration of reagent is highly non-linear. A better response profile and hence a control of pH is claimed for some reagents. Examples include the use of carbon dioxide, or magnesium hydroxide which are self-buffering. A typical titration curve favours multi-stage dosing. Automatic pH meters should be backed up by regular manual pH measurements and should be calibrated frequently.

Use of other wastes, rather than prime raw materials, should be considered as the neutralising agent.

### (e) Solids removal

The removal of particulate matter from effluent can be hindered by fluctuations in flow. A flow balancing facility may be required upstream of any equipment for the removal of particulate matter.

The removal of finely divided suspended solids can be enhanced by the addition of chemical coagulants/flocculants. Similarly, these substances can aid the removal of emulsified organic material.

The addition and mixing of pH control chemicals and flocculants can be made, as necessary, prior to raw effluent entering the solids removal tank.

## Settlement

Separation of up to 90% of the suspended solids can be achieved by settlement.

Settlement is carried out in a clarifier. The clarifier design that is considered to be the most efficient and economical is a circular, mechanically scraped tank. However, depending on the flowrate, one or more pyramidal-type settlement tanks may be appropriate.

The applicant should have identified a suitable treatment/disposal route for the resultant sludge.

Control for settlement processes should include a sludge blanket level indicator and high-level alarm. Where scrapers are used, loss-of-motion sensors should be used.

Sludge consisting of readily biodegradable organics containing sulphur will have a tendency to produce hydrogen sulphide unless properly aerated.

## Flotation

An alternative to sedimentation is using either induced or dissolved-air flotation, although it is less common in the chemical industry. The required tank size is reduced but more ancillary equipment is needed, making the overall capital cost higher.

Controlled release of pressure produces a rising blanket of micro-bubbles as the dissolved air passes out of solution. The bubbles carry suspended solids to the surface of the tank where they are removed by surface skimmers. Retention times are typically of the order of 20-40 minutes at peak hydraulic loading (influent and recycle). Addition and mixing of pH control chemicals and flocculants can be made as necessary prior to raw effluent entering the tank.

Where volatile organic chemicals may be present, an applicant proposing to use a flotation technique should assess the impact of the release to air of any of those chemicals due to the action of aeration.

Applicants should ensure that adequate control is in place to monitor the air supply. The skimmers on the surface can be monitored by loss-of-motion sensors.

## Precipitation

Precipitation should be considered as a technique for removal of certain compounds, such as those containing heavy metals, which could be recycled or which it is more appropriate to dispose of to land than water.

Control of pH, solid particle growth conditions and residence time are some of the key parameters to be considered. (Where multi-stage precipitation is used, solids separation normally occurs between stages.)

An example of a precipitation system is the removal of mercury from waste waters with one or more hydroxide precipitation

stages (at increasing pH), followed by a sulphide precipitation stage with long residence time.

## Dewatering

Dewatering of sludge wastes is a common method of waste volume reduction.

Mechanical dewatering as opposed to gravity thickening is appropriate for many liquid wastes associated with the manufacture and use of organic chemicals.

A variety of dewatering facilities can be employed including: centrifuges, filter-belt presses, filter-plate presses and rotary vacuum filters. The system choice is dependent on cost, space availability and the degree of dewatering required. An additional dose of polyelectrolyte (1-5 kg/tonne dry solid) may be necessary as a dewatering aid. Such dosing should be optimised.

Dewatering facilities should be situated in enclosed buildings and any noxious fumes emitted should be exhausted via a gas cleaning facility. The filtrate may require treatment prior to disposal.

## Filtration

Intermediate or product materials are often isolated as solids. The maximum retention of solids on the filter is required, which, for batch processes, usually involves recycling the initial filtrate until the initial bleeding of solids has ceased. Loss of solids to water should be quantified.

The method of discharging of the solid filter cake varies between each type of filter but it should be demonstrated that the method selected minimises any spillage or loss of solids to the water environment. Means to collect and recycle any spillage should exist that preclude it being flushed to drain.

If the filter requires clean-down, the quantities of solid product lost to the water environment should be defined and shown to be the minimum achievable.

Since the mechanical integrity of the filter medium is crucial to the operation, a means of preventing its failure and consequent loss to the environment is required. This can take the form of a guard filter, collection vessel or an automatic detection and shut-down system.

Where solid impurities are removed from process liquors and become waste, the means for discharging, as well as techniques to minimise their organic contents, and the disposal method should all be justified.

The replacement of filter cloth can generate a significant clean-down stream. Sometimes replacement can be minimised on multi-product plant by storage of used cloths for re-use on each specific product.

For both liquid/liquid separators and liquid/solid separators the retained batch is usually washed, often with a discrete number

of washes. Sometimes the last wash of one batch can be used as the first wash of the next batch to minimise the overall usage. The application should show that this technique is used or that it is inappropriate.

#### (f) Biological treatment

The treatment of biodegradable material by microbial activity requires detailed consideration of the nature of the waste in order to design an appropriate biological treatment system.

Potential problems of process inhibition due to the presence of toxins can be identified by treatability tests.

A biological effluent treatment plant will be acclimatised to the effluent feed and nutrient conditions. Therefore, under normal circumstances, a flow balancing system or buffer tank is required to balance flows and pollution loads to the plant and to allow analysis to check compatibility prior to treatment.

Biological systems may be aerobic or anaerobic. Typical types include: trickle filter beds (biological filtration); rotating biological contactors; fluidised-bed systems; activated sludge; deep shaft and polishing filters.

For aerobic systems, the use of pure oxygen allows better control with varying loads.

For biological treatment the pH of the feed should be kept between 6.5 and 8.5 to ensure optimum biological activity. Consideration should be given to the effect of loss of biomass due to the introduction of toxic compounds, and a stand-by procedure should be developed for such an event. Such a procedure may include maintaining a stock of seed inoculum.

Closed biological systems can reduce volumes of off-gas and odour nuisance.

#### (g) Activated carbon adsorption

Activated carbon columns are employed for the treatment of toxic or non-disposable waste waters and for tertiary treatment following biological oxidation.

Most heavy metals can be removed by use of carbon columns. In order to avoid reduced capacity after regeneration, the carbon should be acid-washed prior to re-use.

Total organic carbon (TOC) can often be reduced by up to 99%.

Powdered activated carbon (PAC) can be added to activated sludge processes to enhance performance. Typical dosage levels are of the order of 20-200mg/l of effluent feedstock.

Its usage results in decreased variability of effluent quality; the removal by adsorption of non-biodegradable organics; and the further degradation of normally non-degradable substances.

When there is a small or intermittent application of PAC, the carbon is disposed of with the excess sludge. Continuous

application at larger plants, however, requires regeneration of the carbon.

Generally granular activated carbon (GAC) is easier to regenerate, but usage of powdered activated carbon (PAC) offers several advantages. These can include: a more consistent effluent quality; usage and recycling can be integrated into the biological treatment facility at minimal capital cost; and usage can also help to reduce, or eliminate in some cases, the problem of nitrification caused by the presence of toxic organics.

#### (h) Ion exchange resins

Ion exchange can be employed for the removal of undesirable anions and cations from a waste water. Cations are exchanged for hydrogen or sodium and anions for hydroxyl ions.

Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. Ion exchange resins are called cationic if they exchange positive ions and anionic if they exchange negative ions.

Treatment of a waste water by ion exchange involves a sequence of operating steps. The waste water is passed through the resin until breakthrough occurs. The bed is then regenerated by backwashing with water and then regenerant prior to re-use. The disposal of regenerant liquors is an important factor in minimising environmental harm.

Macro-reticular resins are employed for the removal of specific non-polar organic compounds. They are capable of removing between 85 and 99% of Schedule 5<sup>(1)</sup> substances from waste streams.

Fouling of resins, especially by unexpected organic compounds, needs to be considered.

#### (i) Electrolytic exchange

Metals can be extracted from aqueous streams by sacrificial exchange. For example, adding zinc to an aqueous solution of lead salts results in the precipitation of lead, zinc being more electropositive than lead.

This process would result in the release of zinc into the aqueous stream. Careful consideration should therefore be given to the concept of BPEO when considering electrochemical exchange techniques.

#### (j) Membrane processes

Membrane processes include: ultrafiltration, reverse osmosis, membrane filtration, and pervaporation. The efficiency of the filtration processes depends upon the difference in size between the pore and the particle to be removed or retained; whilst in reverse osmosis the efficiency depends on how well the membrane rejects the flow of solute whilst allowing the flow of solvent.

These types of process can be used either to clean up the waste water for re-use, or to recover material for recycling. They tend

to be used in specialist applications where the membrane technology has been developed to overcome membrane life and fouling problems.

Pervaporation is a process that uses polymeric membranes for the removal of organic compounds from water. It is suitable for the treatment of waste water containing VOCs and chlorinated solvents. The component to be separated is 'evaporated' from a liquid waste, through a membrane, under vacuum. The separated component is recovered by condensation. A wide variety of organic polymers can be used to remove specific target contaminants. Pervaporation is a technically feasible and economically attractive method for treating waste water contaminated with VOCs, and compares favourably with steam stripping and carbon adsorption.

Pervaporation has been successfully adopted in the following applications:

- pollution control of dilute solutions of hydrophobic solvents (eg 1000 ppm benzene in water);
- solvent recovery from process waste waters; and
- volume reduction of mixed-solvent hazardous waste.

Pervaporation is particularly suited to waste water containing relatively hydrophobic volatile organics such as chlorinated solvents, naphthas, toluene and benzene.

Ultrafiltration, in which the effluent is passed across a semipermeable membrane at elevated pressures, may be used for the removal of organo-halogen and other pesticides. Efficiencies of removal of 95 to 99% have been achieved from effluent containing 500 to 5000 g/l of total pesticides. After concentration the pesticides should be incinerated if recycling is not practicable.

Reverse osmosis is capable of removing hexachlorocyclohexane and malathion from waste waters at 99% efficiency.

### (k) Oxidation techniques

Oxidation techniques may be particularly appropriate for difficult wastes for which biological treatment is not feasible. They could be associated with the process plant rather than a site system.

#### *Wet oxidation*

For aqueous waste, wet air oxidation is generally more energy-efficient than incineration and is capable of oxidising complex molecules, including some pesticides, with up to 99.9% removal efficiencies. However, tests are normally required to confirm or otherwise the appropriateness of this technique.

Wet oxidation is the aqueous-phase oxidation of organic and inorganic compounds at elevated temperatures and pressures using compressed air, hydrogen peroxide or oxygen. In some

systems additional catalysts are required. Temperatures between 100 and 300°C and pressures between 3 and 120 barg are typically required, depending on which wet oxidation system is chosen and the characteristics of the waste being treated.

The oxidation stage can be used either to convert organics to carbon dioxide, water and nitrogen, or to break complex molecules down into simpler ones. The waste stream in the latter case will undergo a secondary treatment (eg biological) to complete the destruction.

The gaseous stream leaving the oxidation unit will sometimes need additional treatment to remove or destroy environmentally harmful compounds before release.

There are some wet oxidation systems that are operated in the critical temperature and pressure region and can produce significant SO<sub>x</sub> (oxides of sulphur) and NO<sub>x</sub> (oxides of nitrogen) releases in the gaseous stream.

Advantages of wet oxidation include:

- releases of nitrogen oxides are virtually eliminated where the oxidation temperature is low;
- releases of dust or inorganic oxides are eliminated; and
- the oxidation is carried out in a closed system, which reduces the risk of release of unconverted material in the event of a process upset such as runaway reactions.

Possible disadvantages include:

- a certain concentration of oxidisable material is required to allow autothermal operation, and below this concentration an extra energy source is required.

Systems using water at supercritical conditions are largely in the demonstration and evaluation stage.

#### *Advanced oxidation process*

Strong oxidants such as hydrogen peroxide with a catalyst and ozone are used to oxidise organic compounds in waste waters to carbon dioxide, water, salts, etc. Promoting these free-radical reactions by use of ultraviolet light or semiconductor photocatalyst materials is termed advanced oxidation.

Use of UV light and an oxidant is more commercially available than the photocatalyst route.

Consideration needs to be given to the effect of partial oxidation and whether resulting gaseous streams need further treatment.

A pH higher than 9 should generally be avoided to prevent the potential formation of toxic phenolic substances.

## Thermal destruction

Non-biodegradable organic material can be treated by thermal incineration. However, the thermal destruction of mixed liquids can be highly inefficient and the waste should be dewatered prior to incineration. Reference should be made to the Waste Incineration Guidance Note IPCGN S2 5.01<sup>(10)</sup>.

### (I) Dissolved material

Dissolved material, primarily inorganic salts, may not be removed at high efficiencies by the techniques described above. Dilution may occur in a site waste-water system and the Inspector should assess whether this is acceptable. Dissolved salts will be removed to some extent in conventional treatment systems such as flocculation and settling. Where specific abatement measures are needed, the options include:

- chemical precipitation, although this may involve substitution of ions rather than removal;
- concentration by evaporation or membrane (see above) systems, with the concentrate passing to separate treatment;
- crystallisation and recovery of solids, also applicable to some organic compounds;
- ion exchange (see above) and recovery; and
- solvent extraction and recovery, particularly of organic material.

## 3.5 Minimisation of waste to land

The aim for all processes covered by this Note should be to prevent the creation of waste containing substances proscribed for release to land or which could cause harm. Where this is not possible, releases should be minimised by attention to raw materials and process routes, and by recycling wastes arising within the process or re-using them elsewhere.

### 3.5.1 General

The key pollutants likely to be present in releases to land can be derived from a knowledge of the process, materials of construction, corrosion/erosion mechanisms and materials related to maintenance, validated as necessary by the appropriate analytical techniques. The presence of substances created by abnormal operation should be identified, since process abnormalities can carry through substances into the solid waste that are not normally present.

Whether recycling is possible will depend on site-specific factors such as the particular fuels, raw materials, products and methods of operation.

Storage of wastes of particular environmental sensitivity, such as halogenated organics, should be avoided unless the materials are fixed or otherwise rendered harmless. High-temperature incineration may be a preferred option.

Substances for disposal to land may include: organic sludges; inorganic fluoride sludges; acidic catalysts; alumina-, cobalt-, molybdenum- and nickel-based catalysts; acid soots; basic sludges and liquors; and leaded sludges. Other substances may include building materials, scrap metal, maintenance items, etc.

### 3.5.2 Techniques

Inspectors should check that dedicated areas are provided for the collection of solid waste and that methods to prevent cross-contamination of wastes or the mixing of incompatible materials are implemented.

All substances produced by the process and disposed of to land on or away from the site should be handled and conveyed on-site so as to prevent spillage, dust release or the generation of odours.

Sludges for which disposal cannot be avoided should be stored in sealed or covered containers wherever practicable, and in a secure bunded area pending on-site or off-site disposal. Recognised methods of on-site disposal of sludges include incineration.

Amine solutions, molecular sieves and catalysts should be regenerated on-site, where practicable, to minimise the frequency of, and amounts for, disposal. This should be compatible with good air and water pollution control. Where necessary they should be returned to the supplier or a third party for regeneration.

Disposal options will depend upon the nature of the sludge. Each solid/sludge will need to be analysed before the best disposal route can be specified. This may include one, or a combination of, the following:

- incineration;
- solidification;
- encapsulation;
- biological composting; or
- landfill.

For example the sludge from hydroxide or sulphide precipitation of metals may be disposed of via the cement encapsulation route.

Where spillage could occur the plant layout should be such that any spillage can be collected and cannot enter any drainage system.

Solids handling includes discharging solid raw materials, conveying them to process, discharging, storing and conveying solid products, and packing. In all cases, equipment design should ensure that there is the minimum of dust generation and reliance is not solely placed upon dust extraction and treatment plant.

Techniques that have proved to be successful in minimising the generation of dust-laden gas streams when handling dusty solids include:

- Manual weighing-out from raw material containers under local extraction.
- When having to charge solids by hand to a vessel charge hole or manway, a local extraction vent outside the vessel rather than ventilation through the vessel, to minimise dust entrainment.
- Charge complete drums of solids by means of flexible fabric seals between drum and vessel, so that there is no net displacement volume or need for extraction.
- Dissolving sacks charged directly to the vessel.
- Enclosed automatic sack or drum handling plant.
- Drum filling devices that fill from the bottom upwards to eliminate the free fall of solids through the air in the drum.
- Attaching the polythene flexible liner of the drum around the neck of the filling device to contain any dust.

Waste skips receiving solids should be on hard standing to allow removal of spillages.

Wastes should be sampled and characterised, which may include a detailed analysis, at appropriate frequency, to ensure that they may be accepted at the waste disposal facility and so that the relevant information can be made available to the next holder as required by the Duty of Care Regulations<sup>(44)</sup>.

### 3.5.3 Contamination of soil and groundwater

Hard surfacing should be provided in areas where accidental spillage may occur, eg beneath prime movers, in storage areas, and in loading areas. The surfacing should be impermeable to process liquors. This also applies to tank bund floors. This will facilitate recovery and clean-up operations and prevent penetration into the ground. As much of the organic sludges as practicable should be recycled for processing (eg by filtration, centrifuging, etc), to minimise the amounts requiring disposal.

Hard surfacing of areas subject to potential contamination should be drained such that potentially contaminated surface run-off is not allowed to discharge to ground and thus cause a breach of the requirements of the Groundwater Directive as noted in Section 1.5.8 of this document. Particular care should be taken in areas of inherent sensitivity to groundwater pollution. Poorly maintained drainage systems are in many cases known to be the main cause of groundwater contamination and surface/above-ground drains are preferred to facilitate leak detection (and to reduce explosion risks).

In addition to sealed bunds, possible measures to reduce contamination from large storage tanks include:

- double-walled tanks; and
- leak detection channels.

The additional measures could be justified in locations of particular environmental sensitivity. Decisions on the measures to be taken should take account of the risk to groundwater, taking into consideration the factors outlined in the Agency document, Policy and Practice for the Protection of Groundwater<sup>(20)</sup>, including groundwater vulnerability and the presence of groundwater protection zones.

The vulnerability of groundwater to contaminants will depend on the natural characteristics of any given site, specifically on the physical, chemical and biological properties of soil and rocks beneath the site. The Environment Agency has produced a series of maps of England and Wales, which provide a guide to potential groundwater vulnerability. Source Protection Zones are intended to aid protection by defining annular zones around each major potable source, including springs, boreholes and wells, based on travel times.

Surveys of plant that may continue to contribute to leakage should also be considered, as part of an overall environmental management system. In particular, operators should consider undertaking leakage tests and/or integrity surveys to confirm the containment of underground drains and tanks.

### 3.6 Suggested good practice

The operating company should consider all relevant abatement techniques in presenting the case for BATNEEC and BPEO.

The simple list in Table 3.1 contains elements that the Inspector should seek on all plants.

**Table 3.1 Good practise: suggested techniques and principles**

Type and source of pollution	Abatement technique
VOCs to air Storage tanks: volatile liquids	Internal or external floating roof tanks or fixed roof tanks to recovery or destruction. Overfill prevention: level measurement and alarms, preferably automatic cut-off.
Transfer of volatile liquids	Vapour balance lines. Bottom filling road/rail tankers. Any net vapour displacement to recovery or destruction; maximum 35 g/m <sup>3</sup> outlet for Class 'B' VOCs.
Controllable vents	Abatement to achievable release concentrations for non-trivial quantities.
Fugitive emissions	Leak detection and repair programme on equipment and fittings handling gases and light organics. Progressive installation (to an agreed programme) of high-integrity equipment on duties where VOCs of 'high' and 'medium' environmental impact are handled.
Intermittent emissions	All occasional vents (safety, maintenance, etc.) ducted to storage/recycle or to destructive device such as flare.
All VOC emissions	Minimisation at source by measures such as closed process systems, high-selectivity processes, recycle or fuel use of purge streams.
Aqueous effluents	Treatment at the process plant of effluents to a quality that may be adequately treated by conventional water treatment plant.
Ground protection	Sealing of ground with impermeable layer where spills or leaks may occur, eg tank bunds.
Land wastes	Minimisation by process design or by recovery and re-use.



## 4 Benchmark release levels

The release levels given are achievable by all new processes using the best available techniques described in Sections 2 and 3. They are applicable to each non-combustion point source. They should not be applied as uniform release limits, but should be assessed to take account of site-specific conditions so as to comply with the requirement to use BATNEEC and BPEO and any relevant environmental quality standards.

### 4.1 Benchmark releases to air

The benchmark levels for releases to air are listed by substance in Table 4.1, for the appropriate process sectors.

Table 4.1 *Benchmark releases to air (mg/m<sup>3</sup>)<sup>(a)</sup>*

Substance	Level (mg/m <sup>3</sup> ) <sup>(a)</sup>				
	Petrochemicals	Nitrogen Compounds	Acids and aldehydes	Sulphur compounds	Monomers and polymers
Acrylamide		5			
Acrylonitrile		5			5
Amines (total as DMA)		10			10
Ammonia	15	15	15		
Benzene	5	5			
Bromine				10	
Butadiene	5				5
Cadmium and cpds (as Cd)	0.1	0.1			
Carbon disulphide		5		5	
Carbon monoxide	100	100	100	100	100
Chlorine			10		10
1,2-dichloroethane					5
Ethylene oxide	5				
Formaldehyde			5		5
Hydrogen bromide			5		5
Hydrogen chloride	10	10	10	10	10
Hydrogen cyanide		2			
Hydrogen fluoride				5	
Hydrogen iodide			5	5	
Hydrogen sulphide	5	5	5	5	
Heavy metals (excl. Hg, Cd)	1.5				
Iodine				10	
Maleic anhydride			5		5
Mercury and cpds (as Hg)	0.1	0.1			
Methyl mercaptan				2	

Nitrobenzene		5			
Organic sulphides and mercaptans		2		2	2
Oxides of nitrogen (total acid forming as NO <sub>2</sub> )	200		200	200	200
Oxides of sulphur (as SO <sub>2</sub> )			200	200	
Particulate matter	20	20	20	20	20
Phenols, cresols and xylols (as phenol)			10		10
Trimethylamine		2			
Vinyl chloride <sup>(b)</sup>					5
VOC total Class A <sup>(c)</sup>	20	20	20	20	20
VOC Total Class B <sup>(c)</sup> (as toluene)	80	80	80	80	80

## Notes

- a The reference conditions applicable to these levels are: temperature 273 K (0°C), pressure 101.3 kPa (1 atmosphere), no correction for water vapour or oxygen.

Where the term "expressed as" is used, a correction should be carried out using the ratio of the atomic or molecular weights of the substances as appropriate.

All releases should be essentially colourless, free from persistent trailing mist or fume, and free from droplets.

Releases from the processes should not give rise to an offensive odour noticeable outside the site where the process is carried on.

Benchmark release levels for incineration are given in the Waste Incineration IPCGN S2 5.01<sup>(2)</sup>.

Benchmark release levels for associated large combustion plant are given in IPCGN S2 1.01<sup>(1)</sup>.

- b OSPARCOM Recommendation 96/2<sup>(1a)</sup> relates to BAT for the manufacture of vinyl chloride monomer and 96/3<sup>(1b)</sup> to suspension PVC. Both these documents are under revision at the time of writing this Note.

For PVC manufacture, the following release rates are achievable:

Emulsion process - total VCM release from all vessel vents 1.0 Kg/tonne PVC

Suspension process - total VCM release from all vents 0.1 Kg/tonne PVC

- c Where possible, releases of VOCs should be individually identified. The VOC concentration levels apply where the following total mass release rates are exceeded:

total Class A 100 g/h

total Class B 5 tonnes/yr or 2 kg/h, whichever is the lower (expressed as toluene)

Releases below these mass emission rates may not be trivial, and so may still require controls and the setting of appropriate release limits.

The use of a release concentration limit is not normally appropriate in the case of a release from an air-deficient saturated vapour space such as a storage tank or process vessel. An approach based on limiting total mass released or mass per unit of production is likely to be more effective.

The term "volatile organic compounds" includes all organic compounds released to air in the gas phase. See also Appendix 1.

## 4.2 Benchmark releases to water

The benchmark levels for releases to water are listed by 'substance' in Table 4.2.

**Table 4.2 Benchmark releases to water (mg/l)<sup>(a)</sup>**

Substance	Level (mg/l)
Total hydrocarbon oil content (IR method)	1-3
Biological oxygen demand (BOD) (5 day ATU @ 20°C)	20-30
Chemical oxygen demand (COD) (2 hour)	100-150
Total nitrogen (as N)	10-15
Suspended solids (dried @ 105°C)	20-30
Chlorinated organic compounds <sup>(b-d)</sup>	See TGN A4 <sup>(a)</sup>

Notes:

- a The levels given here are ranges achievable after effluent treatment and are not release limits. They are given on the basis of flow weighted monthly averages.

For pollutants resistant to biodegradation, achievement of the levels will require isolation at source and separate specialised treatment.

On-site effluent treatment is preferred for these processes. Where discharge to sewer is proposed, the applicant should demonstrate that this option represents BATNEEC/BPEO, taking into account:

- the substances released and their separability and degradability;
- the type of sewage treatment available;
- the security of the sewage treatment system, eg with regard to storm overflow; and
- the relative performance of the available sewage treatment compared with that of the site dedicated option.

Compliance with limits imposed by the sewage undertaker does not guarantee compliance with BATNEEC/BPEO.

- b EC Directive 90/415/EEC<sup>(16)</sup> gives limits for releases to water from the production and use of 1,2-dichloroethane, trichloroethylene, perchloroethylene and trichlorobenzene.
- c OSPARCOM Recommendation 96/2<sup>(17)</sup> includes values for discharges to water from the manufacture of VCM. OSPARCOM Recommendation 96/3<sup>(18)</sup> includes values for discharges to water from the manufacture of suspension PVC. Both these documents are under revision at the time of writing this Note.
- d SI 1989 No 2286 and SI 1998 No 389 give annual mean concentration standards for certain dangerous substances in receiving waters.

## 5 Economic considerations

### 5.1 Introduction

In determining a case, the Agency must translate BATNEEC into conditions to be included in the Authorisation. The BATNEEC criterion requires that a judgement is made, balancing cost against environmental damage. The operator should have constructed a BATNEEC case after examining the range of technically feasible process and/or abatement options.

The cost of controlling releases should not be disproportionate to the environmental benefits delivered. There may be cost savings resulting from changes made to improve environmental performance. BATNEEC is not concerned with the financial health or resources of a particular operator, and excessive costs are viewed in the context of the process and the industry. While techniques and achievable release levels may vary between industry sectors, the same principles apply to all sectors. For existing processes, the timing of improvement programmes may be a factor in the determination of BATNEEC.

The information contained in this section gives background on the economics of the industry and the ability of operators to raise funds for investment as well as an indication of possible abatement costs.

### 5.2 Analytical approach

The petrochemical and large-volume organic processes are not part of a homogeneous industry. There is a wide range of process types and of plant sizes. While certain abatement techniques are common to many processes, variations in the technical duty can result in very large differences in cost per tonne of product or per tonne of pollution abated. There is also considerable variation in the business background to different production processes, and to the margins achieved. It is therefore not possible to provide quantitative guidelines to define when certain abatement techniques entail excessive costs. The review in this Note consists of background analysis to assist in the assessment of BATNEEC proposals.

One element in the analysis is the economics and profitability of the relevant industry subsector. The mechanism by which prices are set and the nature of international competition are important factors.

The second element in assessment of whether costs are excessive is that of estimating the abatement costs themselves. Indicative costs of abatement quoted in this IPC Guidance Note consist of incremental cash costs plus a capital charge. The incremental cash costs include net variable costs of the abatement measure, and additional fixed costs such as maintenance and taxes. Unless stated otherwise, it is assumed that there is no increase in operating labour and allocated site overheads. The annualised capital charge is calculated using a real discount rate of 10% per year over ten years. This approximates to a typical cost of capital rather than to the

opportunity cost to the company. If additional abatement measures are likely to be required in less than ten years, a higher rate of annualisation may be appropriate. Applicants should calculate the costs of abatement in a reasonable and consistent fashion in their applications.

### 5.3 Industry economics

Background information is given below on two main types of processes: basic petrochemicals and commodity polymers. An additional commentary is provided on representative other processes.

#### 5.3.1 Basic petrochemicals

Processes that can be considered as basic petrochemicals include most of those under Section 4.1 of the Regulations<sup>(1)</sup>. Some monomer processes and others also exhibit similar economic features. These include phthalic anhydride, terephthalic acid, acrylonitrile, adiponitrile, ethylene dichloride, vinyl chloride monomer and styrene.

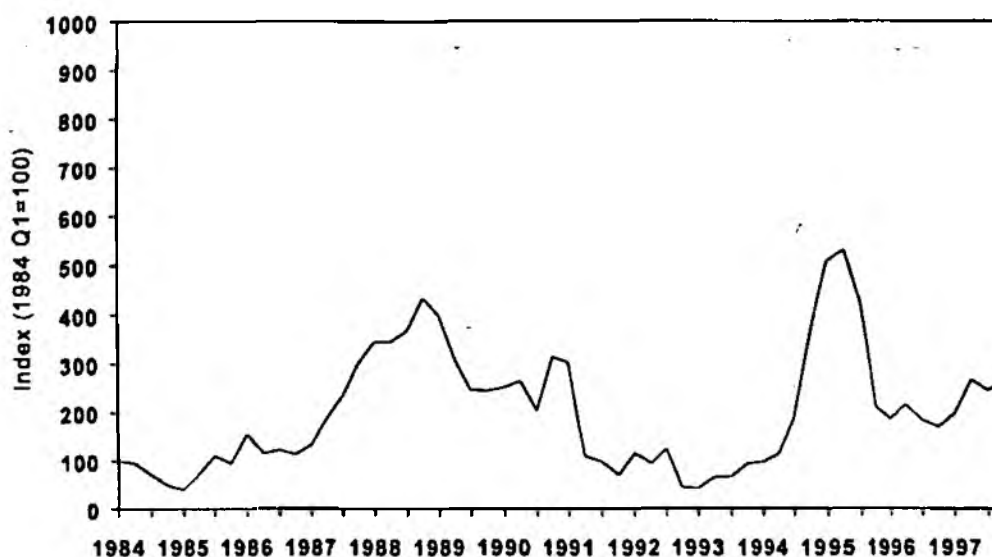
For each process, the number of plants in the UK is typically one to five. Almost all of the plants fall into the category of being large on the criterion of turnover. The operators are large chemical companies or petroleum companies. Many of the plants are relatively old, but most have been periodically revamped in the course of expansions.

Petrochemical processes are based on petroleum feedstocks such as naphtha gas oil, or associated gas. Petrochemical building blocks such as olefins and BTX aromatics (benzene, toluene and xylenes) are converted in downstream processes to other petrochemicals. Final chemical products of the petrochemical industry include polymer resins for processing into plastic products, solvents and surfactants. The 'basic petrochemical' processes reviewed here are typically those in the first or second stage of a petrochemical processing chain. The products are usually commodity intermediates that are supplied to other chemical plants or companies.

Basic petrochemical products are sold on chemical specifications rather than (usually) brand name or performance in use. As a result, competition is focused heavily on price. Within any region, such as Western Europe, different producers have differing costs of production. The differences arise from, for example, variations in scale, in feedstock source and type, and in process plant. The price for a product is related to the cost of production of the incremental source of supply, at the more expensive end of the cost curve. In essence, the basic petrochemical business is characterised by competition on price with cost of production playing a very large part.

The commodity petrochemical business is highly cyclical. This corresponds to some extent to normal business cycles in demand. It is accentuated by the large-scale nature of the fixed

Figure 5.1 Profitability of West European petrochemical and polymer industry



investment, and the understandable tendency for producers to plan new capacity when cash flow is good. With the long lead times of projects, the result is frequently over-capacity, temporarily depressing margins.

The cyclical nature of the business is illustrated in Figure 5.1. This is calculated on the basis of cash cost margins for leader plants for a weighted basket of commodity petrochemicals and polymers. The leader plant is a model that broadly represents the best 20% of the regional cost curve. For less competitive plants than leaders, the cash cost margin may well be negative in the troughs in the business cycle.

Two further features of this industrial sector are relevant. First, producers may be integrated upstream in preceding processing steps or in refining or integrated downstream, perhaps to final product manufacture. Integration can improve the cost competitive position of companies. Care is therefore needed in assuming that the impact of additional costs will be the same for every company producing a certain basic petrochemical. Second, competition is on a regional or even a global basis. Regions with low feedstock costs, primarily the Middle East, may produce basic petrochemicals and export to Western Europe. For several products, the net import to the UK is over 50% of UK consumption. Other products may show a net export. With this direct competition, it may not be possible to pass on incremental costs to customers.

Cash costs of production are of particular importance in setting prices. This is because capital costs will have been written down in the financial accounts for older plants, and are in any case sunk costs. Cash costs of production for Western European leader plants were typically in the range £150 to £450 per tonne for different petrochemicals in 1997. Prices and margins fluctuate with the business cycle. At the peak, most plants generate substantial cash flow. However, when a plant is at the less economic end of the regional cost curve, it may suffer negative cash flow in the troughs of the business cycle.

Conclusions of relevance in assessing whether the costs of

abatement are excessive are as follows.

- At some times in the business cycle, companies in the sector generate substantial cash flow while at other times they may suffer a cash shortage or deficit.
- Special factors such as exchange rate fluctuations can affect profitability.
- It is not meaningful to quote environmental costs as a percentage of margin for a single year; averaging across the business cycle is needed.
- Commodity producers cannot pass on cost increases that apply only to them.
- The position of a plant on the cash cost curve determines whether it breaks even or suffers a significant cash drain in poor times. In practice, this seriously influences companies' decisions on plant closure and exit from the business.

### 5.3.2 Commodity polymers

Commodity polymers include polyolefins, PVC and polystyrene. The polyolefins include low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), high-density polyethylene (HDPE), and variants. Feedstocks to commodity polymer-processes are certain of the basic petrochemicals reviewed above. There are one to five plants for each product in the UK.

The economic dynamics of the commodity polymer business are broadly similar to those for commodity petrochemicals. There is a substantial fluctuation in both prices and margins over the industry business cycle. The nature of the market, however, differs in a number of aspects:

- Consumers are plastics processors of varying sizes rather than (usually large) chemical companies; distribution networks and customer service are particularly important.

- Plastic products compete directly with each other and with other materials in many applications.
- Polymers must satisfy many requirements both for processability and to provide the required attributes of the packaging or other end-product; the product may be supplied compounded in some cases.

Commodity polymers is an increasingly global business, with a move towards large players that focus on certain core business areas. As well as reduced corporate costs, the larger players aim to provide good market coverage and customer support. A number of the major producers in Europe are now joint ventures between companies consolidating a position in specific products.

Western Europe as a whole has been suffering increasing competition from other regions, especially the Middle East with its low-cost hydrocarbon feedstocks. The UK is a large net importer, with imports counting for around half of UK consumption.

With feedstocks priced at market value, the cash costs of production were around £350 to £450 per tonne for the main commodity polymers for Western European leader plants in 1997. The cash cost margin, which takes no account of depreciation or return on capital, has varied over the last decade from negative values to positive margins of over £200 per tonne for Western European leader plants.

The conclusions are the same as those quoted for basic petrochemicals.

### 5.3.3 Other processes

The majority of the processes are influenced to some extent by the petrochemical business cycle. However, the economic characteristics are increasingly modified when:

- a process is several steps downstream from basic hydrocarbon feedstocks, attenuating the effects of the petrochemical cycle; and
- strong technical support and customised applications are a very important part of the business, tending to move pricing from a commodity cost-plus basis to the more performance-oriented area of specialities.

#### (a) Emulsion polymers

One illustrative example in this category is that of emulsion polymers.

Emulsion polymers are principal components in the manufacture of a wide variety of products, including paints and coatings, adhesives, paper, carpet backing, textiles and others. Four major groups are made in Western Europe:

- acrylics (all acrylic, styrene acrylic, vinyl acrylic);
- polyvinyl acetate;
- styrene butadiene (SB);
- vinyl acetate ethylene (VAE).

There are many emulsion polymer plants in the UK. The principal product of the business is a 50 percent solution, except for VAE powders. This has led to many plants being built in each country due to the costs of moving dilute solutions to a very high number of local clients. The business requires a high degree of technical service to meet the demands of such a wide diversity of client needs. Plants are multi-purpose for acrylics and vinyls and single purpose for VAE and SB/SBR latex. Total volumes of emulsion polymers in Europe are over one million tonnes per year, with styrene butadiene latex the largest volume. Many plants are in the 10 to 20 year vintage and are thus in the retrofit category for installing new abatement techniques.

VAE is the product with the highest growth potential among this group, mainly to the adhesives, coatings and powder markets. Recent years have seen an increasing demand for VAE both as a 50 percent solution and spray dried powder form in the construction industries. Spray drying is used in Germany and Holland.

The cash cost of production for VAE in Western Europe varied in 1997 from around £700 per tonne to £920 per tonne, calculated on site-specific data. Cash cost margins were around £200 to £400 per tonne. Although not tied completely to the petrochemical business cycle, profitability does vary with external circumstances. Downturns in construction activity have a serious impact on the emulsion polymer business, for example.

#### (b) Formaldehyde

Another example of an industry sub-sector which is not fully linked to the petrochemical cycle is that of formaldehyde production.

Formaldehyde is one of the most widely used chemicals. The largest use is in resins such as urea formaldehyde, phenol formaldehyde, and melamine formaldehyde. Wood chip products are a major end-use, and producers are often integrated downstream into resin production or even into manufacture of wood products. Other uses of formaldehyde include the production of polyhydric alcohols and of butanediol, although the latter is challenged by new process routes that are based on other feedstocks. Formaldehyde is also one of the feedstocks in the production of MDI, an isocyanate used to produce polyurethanes.

There are six manufacturers of formaldehyde in the UK, with capacities ranging from a few thousand tonnes per year to over 100,000 tonnes per year.

The feedstock for formaldehyde production is methanol, which is itself produced almost exclusively from natural gas. Methanol prices are driven by demand factors, such as MTBE consumption in gasoline, and international supply capability. In 1995, a global imbalance caused European prices of methanol to surge to US \$300 per tonne compared to a more usual US \$100-150 per tonne. Methanol prices do not necessarily follow the petrochemical business cycle, so there is some degree of decoupling from the petrochemical industry.

Table 5.1 Cost of VOC containment: storage and transfer

Abatement technique	Capital cost (£000)	Annualised cost (£)	Cost per tonne VOC (£/tonne)
External floating roof: secondary seal	28	4140	650
Internal floating roof	79	12300	965
Road tanker mods	80	11700	835
Single-stage VRU	710	137650	2900
Plus second-stage VRU <sup>(a)</sup>	115	22700	9550

Notes. a. Incremental.

Table 5.2 Cost of incineration or adsorption of VOC.

Abatement technique	Capital cost (£000)	Annualised cost (£)	Cost per tonne VOC (£/tonne)
Thermal incinerator – no recuperation	490	456	1170
Thermal incinerator – 70% recuperation	586	238	610
Thermal regenerative	720	176	450
Catalytic incineration	630	201	510
Adsorption	1456	315 <sup>(a)</sup>	800 <sup>(a)</sup>

Notes. a. No credit included for recovered VOC.

The cost of formaldehyde production is dominated by the price of methanol, which is usually purchased from third parties. The cash cost of production of 37 percent formaldehyde in Western Europe was around £60 per tonne in 1997, of which variable cost was around £40 per tonne. Large scale purchasers of formaldehyde often agree a price formula that includes the price of methanol. For producers integrated downstream, as many are, this may not eliminate risk as there will be an upward pressure on the price of the finished product, and a downward pressure on margins, if methanol prices surge.

## 5.4 Costs of pollution abatement

Estimates of costs of abatement by different techniques are presented in the research report<sup>(27)</sup> which should be consulted for further details. Some of the estimates are summarised below for illustrative purposes. These are very sensitive to site specific factors. The relative cost ranking of different options may change with the process duty. In all cases, the onus should be on the operator to develop robust cost estimates that correspond to its specific process and circumstances.

### 5.4.1 VOCs from tanks and transfers

Control of evaporative losses from tanks and in loading operations is a common requirement. The cost data given in table 5.1 are based on liquid with a vapour pressure of 40 kPa at operating conditions, storage in two tanks of 5,000 m<sup>3</sup> each, and transfer of 100,000 tonnes per year. Four road tankers are included in this scope. A nominal credit of £1.50 per tonne is

given for saved VOC.

### 5.4.2 VOCs from continuous vents

There are many techniques for the destruction or recovery of VOCs in continuous vents. The economic data presented in Table 5.2 relate to incineration or recovery by carbon adsorption of around 2000 mg/m<sup>3</sup> of oxygenated organic in a stream of 25,000 m<sup>3</sup>/hour.

As well as site-specific factors such as plant layout, the flowrate and VOC concentration affect the economics dramatically. Table 5.3 illustrates this.

### 5.4.3 Fugitive emission of VOCs

Fugitive emissions of VOCs, occurring as leaks from equipment and fittings, may be tackled in two main ways. For the first selection of high-integrity equipment and fittings it is difficult to split out the true incremental costs. The second approach is to improve maintenance with a leak detection and repair (LDAR) programme.

A simple LDAR scheme, involving annual inspection of gas and volatile liquid service components, is estimated to result in a net annualised cost of £12,000 per year or £760 per tonne VOC. This is for a typical plant handling 20,000 tonnes per year of gaseous hydrocarbon streams and 30,000 tonnes per year of volatile liquids.

**Table 5.3 Cost of incineration or adsorption: sensitivity to process duty**

Abatement technique	VOC (mg/m <sup>3</sup> )	Flow (m <sup>3</sup> /hour)	Annualised cost (£000)
Thermal incinerator 70% recuperation	2000	25000	238
Thermal incinerator 70% recuperation	10000	5000	50
Adsorption	2000	25000	315
Adsorption	10000	5000	175

#### 5.4.4 Control of SO<sub>2</sub> emissions from combustion

Combustion processes may form part of petrochemical and large-volume organic compound processes. If SO<sub>2</sub> arises from combustion, fuel switching is a possible means of abatement. The cost of a fuel switch from high-sulphur fuel oil would be around £300 to £500 per tonne of SO<sub>2</sub>, excluding costs of converting burners.

#### 5.4.5 Control of NO<sub>x</sub> emissions from combustion

Low NO<sub>x</sub> burners or other combustion modifications are generally accepted as good practice and the incremental cost on new plant is small. An indicative cost is given in Table 5.4 for a retrofit on an existing plant. Flue gas treatment techniques are more costly but, with other measures, could be considered BAT. The cost estimates in Table 5.4 are for Selective Non-Catalytic Reduction (SNCR) and Selective Catalytic Reduction (SCR) on the flue gas from a 40 MW fired heater.

#### 5.4.6 Water treatment

Effluent from processes often passes to a site waste-water treatment plant. Incremental costs arising from the subject process are difficult to identify. As illustration of process-based aqueous effluent, the costs of treatment of effluent with a

high organic content are shown in Table 5.5. The flow is 5 m<sup>3</sup>/h with organics at 5000 mg/l.

#### 5.5 Impact on costs of production

It is difficult to assess the costs of abatement on a group of processes, or even on one process, because the requirements and the costs will be site-specific. To put some of the control techniques into an economic context, a simple generic case is taken as basis. This does not represent a specific process, but has several elements that occur in petrochemical facilities. The generic case is shown in Table 5.6. The process duties for each abatement technique, and the costs of control, are not necessarily the same as those used for illustration in Section 5.4.

The illustrative abatement techniques are as follows.

For control of losses from storage and loading, three types of techniques are considered. One is the installation of an internal floating roof on the four storage tanks. A single-stage vapour recovery unit (VRU) and a second VRU stage are the other two techniques.

Fugitive losses are taken to be controlled by leak detection and repair (LDAR). Two levels are examined. Level I requires annual inspection of gas and liquid components, while Level II is more stringent.

**Table 5.4 Cost of NO<sub>x</sub> abatement**

Abatement technique	Capital cost (£000)	Annualised cost (£000)	Cost per tonne NO <sub>x</sub> (£/tonne)
Low NO <sub>x</sub> Burners	190	38	1200
SNCR	540	171	3600
SCR	1865	417	6950

**Table 5.5 Cost of treatment of a high-organic effluent**

Technique	Capital cost (£000)	Operating cost (£000 per annum)	Annualised cost (£000 per annum)	Unit cost (£/m <sup>3</sup> )
Incineration	4000	1750	2400	60
Wet air oxidation	5000	360	1170	29
Supercritical water oxidation	7000	690	1830	46



Table 5.6 *Generic petrochemical plant*

Element	Unit	Basis
Production (liquid of moderate volatility)	tonne per year	200000
Feedstock (liquid at ambient conditions)	tonne per year	100000
Purge stream with air	m <sup>3</sup> /h g/m <sup>3</sup>	50000 5
Difficult aqueous stream with organics	m <sup>3</sup> /h	5
Main fired heater/furnace	MW	35

A hydrocarbon purge in an air or inerts stream is assumed to arise from the generic process. In practice, this is not perhaps completely characteristic of most petrochemical plants, where inerts volumes are usually small. It is possible that streams with a significant organic content could find a home in the site boiler or other heaters, unless there are technical or regulatory problems with this. For the purposes of economic analysis, the abatement technique considered is that of thermal oxidation with energy recovery.

Application of selective catalytic reduction (SCR) to abate NO<sub>x</sub> emissions from a process furnace is an unusual requirement, although regulators elsewhere in Europe have requested it when considering a new ethylene cracker application. Some processes produce relatively small volumes of difficult aqueous wastes with a significant organic content, such as from caustic scrubbing. The technique considered to abate this is wet air oxidation.

Finally, a nominal cost is included for coating the floors of storage tank bunds with concrete that is impermeable to

hydrocarbons, as an example of ground protection measures.

All these are add-on techniques rather than representing any form of fundamental redesign. It is impossible to generalise on the costs of waste minimisation and recycling.

The costs of the selected abatement techniques on the generic petrochemical plant are shown in Table 5.7.

### 5.6 Economic implications of pollution control costs

The heterogeneous nature of the process sector, and the cyclical fluctuation in prices and margins, make it difficult to suggest cut-off points for excessive costs.

Fixed investment typically ranges between 1 and 6% of gross revenues, if major acquisitions and expansions are omitted. Operating profits also vary widely over the business cycle, with a typical range of -5% to 15% (positive) of gross revenue.

Table 5.7 *Costs of abatement: generic petrochemical plant*

Technique	Capital £000	Annualised cost £000 pa	Cost/tonne of VOC £	Cost/tonne of product £
VOC				
Internal floating roof	157	25	964	0.12
Loading VRU	1000	190	2000	0.95
Loading VRU II <sup>(a)</sup>	160	31	6715	0.16
Fugitives I	40	7	95	0.03
Fugitives II <sup>(a)</sup>	100	53	4400	0.27
Thermox on purge	875	784	400	3.92
Other				
SCR	1870	418		2.09
WAO	5000	1170		5.86
Ground protection	50	3		0.01

Notes. a. Incremental costs of second stage shown

## 6 Monitoring

### 6.1 General

There is an expanding series of HMIP and Environment Agency Technical Guidance Notes on monitoring, containing information on theory and methodology, and providing technical information on monitoring techniques (see Associated publications at the end of this Note).

Conditions in the Authorisation should require the results of all monitoring to be reported in line with the IPC standard Authorisation format.

The applicant should provide a clear statement of the potential for release of all substances that might cause harm to the environment, and propose an unambiguous set of procedures for measuring or otherwise estimating releases of key pollutants.

Information should be provided on release routes, methods of relevant monitoring or sampling and analysis, and periods and frequency of assessment. Evidence should be provided that quality assurance procedures are in place to ensure that all monitoring and test results are sufficiently accurate and reliable (for example by reference to British/international standards and accreditation with the United Kingdom Accreditation Service (UKAS)). Reference should be made to the application when setting standards of release in Authorisations to ensure that such conditions are assessable by means described by the applicant, and are properly enforceable.

The requirements and frequency of sampling, analysis and monitoring are site- and/or process-specific, influenced by consideration of the anticipated volume and composition of the waste streams.

### 6.2 Monitoring releases to air

For continuous monitoring, release concentration levels are given on the basis of 95% of the hourly average readings for each rolling 24 hour period not exceeding the value and the maximum hourly average not exceeding 150% of the value. For non-continuous monitoring, the levels refer to the sampling period appropriate to the test method. In order to relate emission concentrations to mass releases, it will be necessary to measure or otherwise determine the gas flow. Additionally, in order to relate measurements to reference conditions, temperature will need to be determined. Determination of oxygen or water vapour content may also be required. All such measurements should be recorded.

Where appropriate, continuous monitoring techniques should be used, commensurate with the limitations and accuracy of continuous monitors. When continuous monitoring is not appropriate or available, non-continuous monitoring should be undertaken, together with continuous surrogate measurements where applicable.

In requiring the use of continuous monitoring for any given release point, several factors should be taken into account. These include the size of the process and its releases, the value of monitored versus calculated results (eg by using proven mass balance/factoring methods) and the usefulness of continuous records where a release may be time-dependent, such as changing over production cycles/catalyst life, etc.

The Agency has established its Monitoring Certification Scheme (MCERTS). Continuous emission monitoring systems should be expected to meet the performance standards published under the Scheme. Manual stack testing should be carried out in accordance with the separate MCERTS performance standards being developed for non-continuous monitoring which include the use of the Agency's standard reporting formats.

Wherever a combustion process (other than flaring) is used for the destruction of hydrogen sulphide or hydrocarbons, its effectiveness should be demonstrated indirectly by continuously monitoring the temperature and oxygen content of the exhaust gas. Visual and olfactory assessments of releases from incinerators, flares, furnaces and other sources liable to cause a nuisance emission should be made when appropriate, particularly during upset/start-up/shut-down conditions. Remedial action should be taken immediately in the case of adverse observations and the cause of the release and action taken should be recorded in the log book.

Additionally, all flare systems should be equipped with adequate monitoring and control systems necessary to operate smokelessly and to be so observed at all times under non-emergency conditions. Such systems should include flow measurement, for which proven non-intrusive systems at the flare base are available, with automatic steam control, luminosity measurement with automatic steam control, remote visual observation using colour TV monitors in relevant plant control rooms with access to steam control, pilot flame detection, etc. Inspectors should take into account the size and nature of flare installations in deciding which of the above features should be used.

The site should be equipped with suitable portable hydrocarbon monitors so that all process vents and possible sources of fugitive losses are checked to assess hydrocarbon emissions from the site as a part of the leak detection and repair (LDAR) programme. The instrument(s) should also be used to check for leaks and other irregular venting at times of plant maintenance and shut-down. An assessment should be made of the total hydrocarbon emissions from the site on a regular basis to a programme agreed with the Inspector. Records should be kept of the individual contributions to each total. The activities of the site LDAR programme should also be retained as records for examination by the Inspector. Monitoring should be undertaken during commissioning, start-up, normal operation, and shut-down unless the Inspector agrees that it would be inappropriate to do so. All final releases to air should be

essentially colourless, free from persistent trailing mist or fume and free from droplets.

Where Inspectors are not satisfied with the amount of information available about emissions, a short-term monitoring exercise may be appropriate as part of an improvement programme.

### 6.3 Monitoring releases to water

Continuous monitoring and flow proportional sampling for releases to water are always preferable but the use of a fixed interval or time proportional sampler for flowrates of less than 1 litre per second may be acceptable. Spot sampling may be used for audit or enforcement purposes.

Monitoring of process effluents released to controlled waters and sewers will commonly be made for the following:

- flowrate;
- pH;
- temperature; and
- TOC (surrogate for COD/BOD).

Samples should also be monitored for appropriate other parameters such as those below, over relevant time periods, typically daily, weekly or monthly depending on circumstances:

- COD;
- hydrocarbon oil;
- ammoniacal and total nitrogen;
- suspended solids;
- phenols;
- sulphides;
- dissolved oxygen (where justified by nature of receiving water); and
- metals (typically Cd, Hg, Cr, Ni, Zn, Cu, As).

In addition to the regular monitoring carried out by the operator to demonstrate compliance with the release limits set, the operator should have a fuller analysis carried out covering a broad spectrum of substances to establish that all relevant substances have been taken into account when setting the release limits.

Where Inspectors need to obtain more understanding of the performance of an effluent treatment plant (ETP), a short-term monitoring exercise to provide information about inputs to the ETP may be appropriate as part of an improvement programme.

### 6.4 Monitoring releases to land

The applicant should record and advise the Agency of the quantity and composition (including prescribed substances) of waste released to land. In addition the applicant should have written procedures which ensure that releases are handled, treated and disposed of in an approved manner, and specify how the accumulation and storage of waste are controlled.

The frequency of analysis of the waste is site- and/or process-specific, influenced by considerations of the anticipated quantity, its frequency of despatch from the site, physical form, containment (for transport) and composition. Applicants should be aware that the Agency will wish to be satisfied that analyses should be sufficient to ensure that wastes are acceptable under the terms of the waste management licence of the facility where they are to be disposed of and fulfil the waste description requirements of the Duty of Care.

### 6.5 Environmental monitoring

The impact of the process on the environment will be affected by the quantity and form of the releases, and by the site's location. Inspectors should assess the extent to which process releases have been rendered harmless and decide whether environmental monitoring will be necessary.

For major sites it is considered BAT that some form of environmental monitoring is carried out for releases to air, primarily to confirm compliance with air quality standards, but also to confirm environmental dispersion modelling. Many already operate such monitoring or contribute to joint monitoring carried out by other local operators or agencies. Inspectors should require operators to propose monitoring that is appropriate for the quantity and form of the releases and for the site's location. Such programmes typically commence with the use of a suitably designed grid of passive diffusion adsorption tube sampling sites. Suitable adsorbents are available for most pollutants, including SO<sub>2</sub>, NO<sub>x</sub>, and a range of VOCs (eg benzene). The technique provides an economical method of identifying any environmental "hot spots" and screening to determine whether additional, more accurate and elaborate methods may be required.

### 6.6 Groundwater impact

Where on-site disposals are made, or where there are discharges to groundwater, either directly or indirectly, the requirements of the Groundwater Directive for "prior investigation" of the potential effects on groundwater, and "requisite surveillance" need to be addressed. The form that these will take will depend on circumstances, but it may be appropriate to include a structured programme of groundwater monitoring eg using borehole monitoring.

In addition, where there is reason to suspect that leakage of chemicals to ground may have occurred or may be occurring, a programme of investigations should be instigated and preferably agreed with the Agency (some activities may require the Agency's prior consent).

For many sites it will be appropriate to incorporate a programme of background monitoring of groundwater to ascertain whether the process has given rise through time to groundwater contamination via leaking pipes, accidental spills, contaminated run-off, etc. This is over and above any monitoring required to monitor the effects of specific on-site disposals of solids or liquids on groundwater. Owing to the lengthy residence time and differing modes of transport and degradation in the underground environment, such monitoring is likely to be long-term and should be adapted to the types of contaminant that could be present in the potential discharges. It is essential to include background monitoring of groundwater that has not been affected by site processes (normally up-gradient in the hydraulic sense) to determine objectively the degree of contamination that may be attributable to site processes.

In setting out a programme of investigations, and when interpreting the results, operators should take account of the specific risks to groundwater and seek advice from the Agency in cases of uncertainty.

## **6.7 Records and reporting**

Inspectors shall have regard to the instructions on:

- reporting and monitoring, and
- records and notifications related to incidents, given with the IPC standard Authorisation format.

# Appendix 1 Volatile Organic Compounds

## A1.1 Introduction

Volatile organic compounds (VOCs) are of serious environmental concern because of the harmful or offensive properties that they exhibit in varying degrees. These include:

- direct toxicity to human health and other eco-systems;
- contribution to photochemical ozone creation at ground level with consequent harmful effects;
- destruction of stratospheric ozone;
- contribution to global climate change; and
- sensory effects such as malodour.

The harmfulness of VOCs varies greatly, not only because the individual and combined significance of these properties exhibits wide variation between substances, but also because it is dependent on the presence of the substance in the environment. This is related to mass release rate and subsequent dispersion and to the environmental persistence and fate of the substance under prevailing conditions.

## A1.2 Categorisation

In order to enable Inspectors properly to assess applications for processes that release VOCs, it is necessary to categorise VOCs according to their harmfulness.

Substances such as benzene, vinyl chloride and 1,2-dichloroethane pose serious health risks to humans and are regarded as highly harmful. These are given individual, very low achievable levels of emission in guidance.

Some other VOCs carry a lesser but still significant health risk or may contribute substantially to photochemical ozone creation or stratospheric ozone destruction or global warming. These are regarded as of medium harmfulness and are allocated to Class A. They will include the substances listed in the Montreal Protocol<sup>(1)</sup>, the phase-out of which is covered by EC Regulations 594/91, 3952/92, 2047/93 and 3093/94.

The remaining majority of VOCs are of low harmfulness but are also prescribed substances whose release must be prevented or minimised. These are allocated to Class B.

The definition of "harm" given in the Environmental Protection Act 1990 includes offence to any of man's senses. Odorous VOCs may be offensive at extremely low concentrations and this property may indicate the need for very tight control of a substance that would otherwise be categorised as of low harmfulness.

The research report *The Categorisation of Volatile Organic Compounds* (DOE/HMIP/RR/95/009)<sup>(2)</sup> provides a method of

categorisation, information on the properties of some 500 VOCs and a summary table of resulting categorisations.

In seeking to categorise a VOC, Inspectors should first search the summary table of categorisations. If the VOC is not included, the method and decision tree given in the research report should be used to arrive at a conclusion supported as well as possible by information from established sources. These include the *Registry of Toxic Effects of Chemicals*, the "CHIP" list<sup>(3)</sup>, the Montreal Protocol<sup>(1)</sup> and Sax's *Dangerous Properties of Industrial Materials*.

Knowledge of the harmful effects of VOCs is developing and there may be occasional differences of experts' opinions on the precise interpretation of information. In these few instances, it will be prudent to adopt the more cautious view.

## A1.3 Achievable Benchmark Levels

The levels of emission that can be achieved are dependent on factors that include the prescribed process itself, the VOC concerned and the abatement method used. Before abatement equipment is considered, the operator should review the process to determine whether the emission can be reduced by changes in equipment or operating conditions. It may also be possible to substitute with a less harmful or less volatile compound.

Where possible, process- and substance-specific achievable levels of release are given in Table 4.1 of this Note.

A BPEO/BATNEEC assessment<sup>(5)</sup> should be made wherever possible to determine an acceptable release level. However, in the absence of sufficient information or where it is agreed by the Inspector that an assessment is not possible, the following guidelines may be used to provide a practical approach to setting limits. Inspectors should also consider all relevant information contained in applications and other appropriate sources when they set VOC emission concentration or mass limits in authorisations.

- The benchmark release concentrations given below should be aimed for where the following mass release limits are exceeded:
- Total Class A 100 g/h
- Total Class B (expressed as toluene) 2 kg/h
- Releases below these mass emission levels may not be trivial, and so may still require controls and the setting of appropriate release limits.
- Highly harmful VOCs pose major human health risks and have individual guidance levels given in Table 4.1 of this Note.

- For Class A compounds, state-of-the-art abatement techniques can achieve a benchmark release level of 20 mg/m<sup>3</sup> for continuous releases.
- Some VOCs cause significant malodour problems even at very low concentrations after dispersion, and limits lower than Class A compounds may be required.
- Class B compounds are those of low environmental harmfulness such as acetone and toluene. Toluene has been used as a reference material as it is a common Class B solvent. If levels were expressed as total organic carbon (TOC), the mass concentration limit, particularly for halogenated compounds, would be too lax as the compound may have a high molecular weight relative to its number of carbon atoms.

The Class B benchmark level has been set at 80mg/m<sup>3</sup> toluene based on abatement techniques involving adsorption with activated carbon.

The benchmark release level for a Class B substance may be determined by multiplying the molecular weight of the pollutant by a factor of 0.87 to give the release level in mg/m<sup>3</sup>.

For mixed streams the release level may be calculated by summing the class levels multiplied by their respective mass fractions.

- The above is for guidance on setting release levels only and not for monitoring those releases. Monitoring would be expected to be for individual substance or for TOC.

HMIP Technical Guidance Note M2<sup>(1)</sup> gives more information on monitoring techniques.

- The use of a release concentration limit is not normally appropriate in the case of a release from an air-deficient saturated vapour space such as storage tanks for solvents or process vessels. An approach based on limiting total mass released or mass per unit of production is likely to be more effective.
- In some processes, the VOCs released to air may well consist of partial oxidation products rather than defined compounds that can be classified as above. In such cases an approach based on a TOC release concentration is likely to be more effective. Reference may be made to IPCGN S2 5.01<sup>(1)</sup> and the release emission concentrations used should take into account the harmfulness of the products that are released.

# References

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The Environmental Protection (Amendment of Regulations) Regulations 1991. SI 1991 No 836, ISBN 0-11-013836-8  
  
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The Environmental Protection (Prescribed Processes and Substances, etc) (Amendment) (Hazardous Waste Incineration) Regulations 1998. SI 1998 No 767, ISBN 0-11-065758-6
- 2 Integrated Pollution Control: A Practical Guide. (DETR) April 1994, ISBN 1-85112-021-1  
  
Guidance Notes to Applicants for Authorisation - processes prescribed for regulation by the Environment Agency, available from the Agency
- 3 Monitoring Emissions of Pollutants at Source HMIP Technical Guidance Note (Monitoring) M2 (HMSO) January 1994, ISBN 0-11-752922-2
- 4 Guidelines on Discharge Stack Heights for Polluting Emissions. HMIP Technical Guidance Note (Dispersion) D1. (HMSO) June 1993, ISBN 0-11-752794-7
- 5 Best Practicable Environmental Assessments for Integrated Pollution Control. HMIP Technical Guidance Note (Environmental) E1. (TSO) 1996
- 6 Released Substances and their Dispersal in the Environment. Environmental Analysis Cooperative (HMSO) 1996 ISBN 0-11-702010-9
- 7 EC Directive on the Combating of Air Pollution from Industrial Plants (framework). 84/360/EEC (OJL188, 16/7/84)
- 8 Speciality Organic Chemicals. IPC Guidance Note S2 4.02. (TSO) 1998, ISBN 0 11 310 1546
- 9 European Council Directive on the Limitation of Emissions of Certain Pollutants into the Air from Large Combustion Plant. 88/609/EEC as amended by 94/66/EC
- 10 The Air Quality Standards Regulations 1989. SI 1989 No 317, ISBN 0-11-096317-2
- 11 The Air Quality Regulations 1997. Statutory Instrument 1997 No 3043
- 12 The United Kingdom's Programme and National Plan for Reducing Emissions of Sulphur Dioxide and Oxides of Nitrogen from Existing Large Combustion Plants. Department of the Environment, 20 December 1990
- 13 Protocol to the 1979 Convention on Long Range Transboundary Air Pollution on Further Reduction of Sulphur Emissions. Oslo 1994
- 14 Reducing Emissions of Volatile Organic Compounds (VOCs) and Levels of Ground Level Ozone: A UK Strategy. DETR, Ashdown House, 123 Victoria Street, London SW1E 6DE
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- Good Practice Guides (relevant selection):
- GG12 Solvent Capture for Recovery and Re-Use from Solvent-Laden Gas Streams
- GG37 Cost-Effective Separation Technologies for Minimising Wastes and Effluents
- GG54 Cost-Effective Membrane Technologies for Minimising Wastes and Effluents
- GG100 Solvent Capture for Recovery in Practice: Industry Examples
- GG101 Reducing Vacuum Costs
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- 37 Technical Guidance Note (Abatement) A1, Guidance on Effective Flaring in the Gas, Petroleum, Petrochemical and Associated Industries. HMSO, November 1993, ISBN 0-11-753204-5
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- CIRIA/Environment Agency Joint Guidelines: Concrete bunds for oil storage tanks
- CIRIA/Environment Agency Joint Guidelines: Masonry bunds for oil storage tanks.
- CIRIA/Report No 163, Construction of Bunds for Oil Storage Tanks
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- 41 Pollution Prevention Measures for the Control of Spillages and Fire Fighting Run-off. PPG18. Environment Agency
- CIRIA Report No 164 Design of Containment Systems for the Prevention of Water Pollution from Industrial Incidents
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- The Controlled Waste Regulations 1992. SI No 588, ISBN 0-11-023588-6
- The Environmental Protection (Duty of Care) Regulations 1991. SI No 2839, ISBN 011-015-8539
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- 46 The Chemicals (Hazard Information) and Packaging Regulations Approved Supply List, (TSO), ISBN 0-11-882156-3



# Abbreviations and definitions of terms used

ACH	Acetone cyanohydrin	H <sub>2</sub> S	Hydrogen sulphide
ACN	Acetonitrile	HSE	Health and Safety Executive
AMC	2-Aminomethylcyclopentylamine	IPC	Integrated Pollution Control
API	American Petroleum Institute	IPCGN	Integrated Pollution Control Guidance Note
BAT	Best Available Technique(s)	ICPD	Large Combustion Plant Directive
BATNEEC	Best Available Techniques Not Entailing Excessive Cost	LEL	Lower explosive limit
BPEO	Best Practicable Environmental Option	LDAR	Leak detection and repair
BOD	Biological oxygen demand	LDPE	Low-density polyethylene
CAA	Cuprous ammonium acetate	LLDPE	Linear low-density polyethylene
CFCs	Chlorofluorocarbons	MEHQ	Methyl ethyl hydroquinone
CHP	Combined heat and power	MEK	Methyl ethyl ketone
CIGN	Chief Inspector's Guidance Note	MELA	Monoethanolamine
CO	Carbon monoxide	MIPK	Methyl isopropyl ketone
COD	Chemical oxygen demand	MMA	Methyl methacrylate
CPI	Corrugated plate interceptor	MTBE	Methyl tertiary butyl ether
DACH	1,2-Diaminocyclohexane	NBR	Nitrile butadiene rubber
DCE	1,2-Dichloroethane	NMP	n-methylpyrrolidone
DELA	Diethanolamine	NO <sub>2</sub>	Nitrogen dioxide
DMA	Dimethylamine	NOX	A mixture of nitric oxide and nitrogen dioxide
DMAC	Dimethylacetamide	PAN	Polyacrylonitrile
DMAE	Dimethylaminoethanol	PEB	Polyethylbenzene
DMCHA	Dimethylcyclohexylamine	PMMA	Poly(methyl methacrylate)
DMF	Dimethylformamide	PPI	Parallel plate interceptor
EB	Ethylbenzene	PTA	Pure terephthalic acid
EP	Electrostatic precipitator	PVC	Poly(vinyl chloride)
EPA90	The Environmental Protection Act 1990	SCR	Selective catalytic reduction
EPS	Expandable polystyrene	SNCR	Selective non-catalytic reduction
ETBPP	Environmental Technology Best Practice Programme	SRU	Sulphur recovery unit
ETP	Effluent treatment plant	SWS	Sour water stripping
HCFCs	Hydrochlorofluorocarbons	TELA	Triethanolamine
HDPE	High-density polyethylene	TMA	Triethylamine
HMD	Hexamethylenediamine	TVP	True vapour pressure
HMI	Hexamethyleneimine	TOC	Total organic carbon
HMT	Hexamethylenetriamine	VCM	Vinyl chloride monomer
HMIP	Her Majesty's Inspectorate of Pollution (former)	VOC	Volatile organic compound
		VRU	Vapour recovery unit

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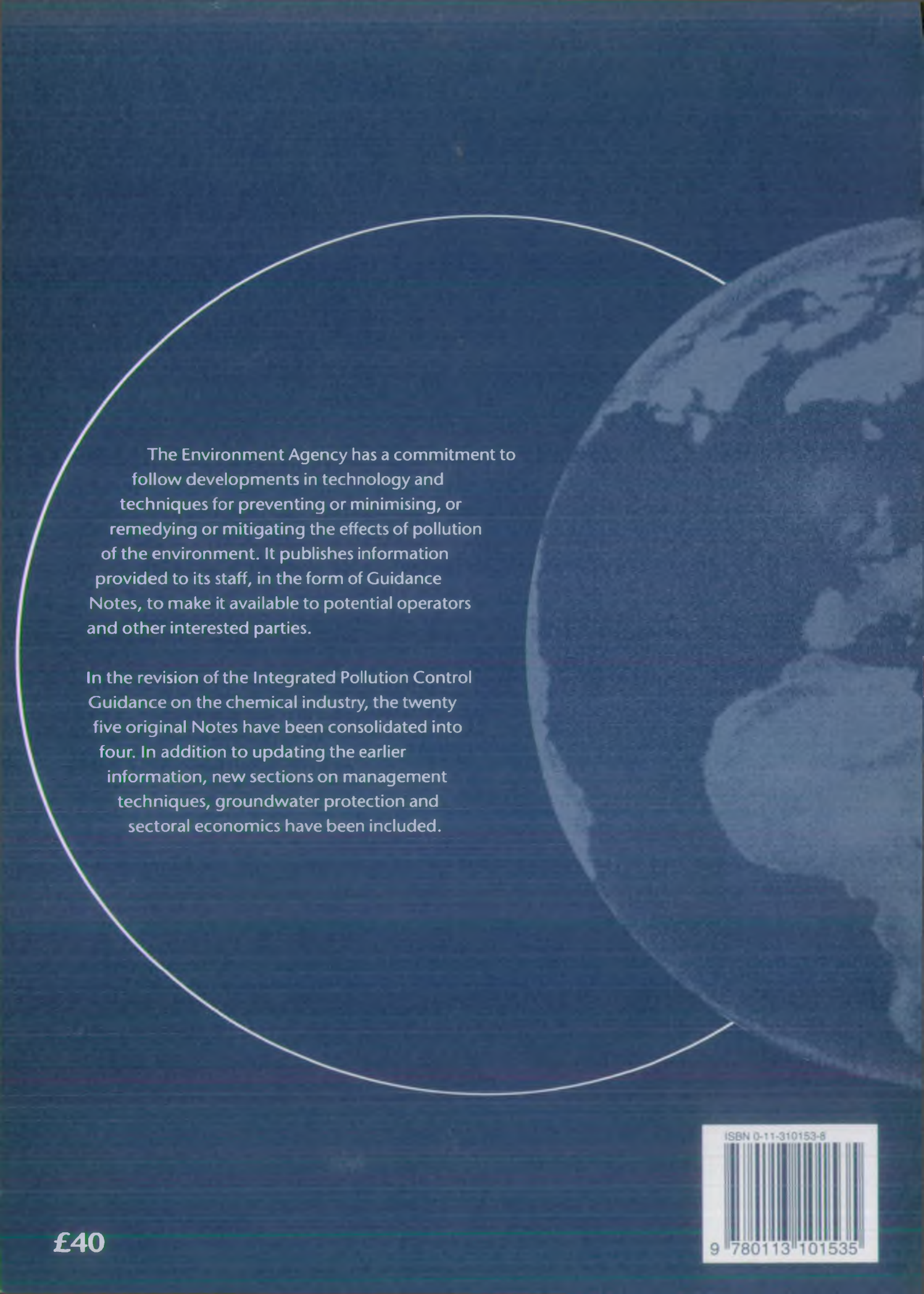
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