7   ETHYLENE OXIDE AND ETHYLENE GLYCOLS

7.1   General information

Although ethylene oxide (EO) and ethylene glycols (EG) can be produced separately, nearly all European installations produce a mix of products in integrated plants. These production processes are therefore considered together in this chapter.

Ethylene oxide is an important chemical intermediate used in the production of ethylene glycols (as described here), but also detergent ethoxylates, ethanolamines, glycol ethers and polyols. A very small portion of the EO produced is employed directly as a sterilising agent and as a fumigation chemical. It is produced by the oxidation of ethylene. Ethylene glycol is a collective term that refers to monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG). It is produced by reacting ethylene oxide with water. MEG is mainly used for the manufacture of polyester fibres and polyethylene terephthalate (PET); other uses include as an anti-freeze in cooling systems (e.g. car radiators). DEG is used in many applications like in the production of unsaturated polyester resins and in polyurethane systems, and TEG is used mainly in the production of polybutylene terephthalate foils and for gas purification and drying. [90, REBSDAT et al. 2012].

Industrial production of EO started in 1937 with a Union Carbide process based on ethylene and air. In 1958, oxygen (rather than air) processes were introduced by Shell Development Company, and now most European EO plants are based on pure oxygen feedstock. Ethylene glycols are produced by reacting EO with water. About 40 % of the European EO produced is converted into glycols, although worldwide the figure is about 70 %. [41, CEFIC 2010].

Although production plants can be designed to produce either just high-purity ethylene oxide or just ethylene glycols, it is more normal for a plant to produce a mixture of the two. This reflects the fact that the production of ethylene glycol is a major end use for ethylene oxide, and that the handling and transportation of ethylene oxide is hazardous. However, there are also process integration drivers for producing a mixture of the two at the same location - the manufacture of ethylene oxide inevitably results in the formation of some ethylene glycols, and the excess heat generated during the production of ethylene oxide can be used to offset the energy demand associated with the dewatering and separation of ethylene glycols.

The total European production capacity of EO (ex reactor) is about 3 000 kt/yr.

Table 7.1:   European producers of ethylene oxide and ethylene glycol

Country	Company	Location	EO capacity* (kt/yr)
Belgium	BASF	Antwerp	500
Belgium	Ineos Oxide	Antwerp	420
France	Ineos Oxide	Lavera	220
Germany	BASF	Ludwigshafen	345
Germany	Ineos Oxide	Dormagen	290
Germany	Clariant	Gendorf	240
Germany	Sasol	Marl	216
The Netherlands	Shell	Moerdijk	305
The Netherlands	Dow	Terneuzen	170
Poland	PKN Orlen	Plock	Approx. 100**
Spain	IQOXE	Tarragona	130
Sweden	Akzo Nobel (S)	Stenungsund	115
Total			3 050
* Nominal 2014 EO capacities. ** 2012: EO 27 kt + glycols 74 kt [115, Orlen 2012].			

EO and EG are sold on chemical specification, and competition between producers is heavily geared towards price and margins are low. The EG market is global and prices are strongly influenced by the price of ethylene. In 2010, the global market of MEG was 18 900 kt, growing on average at 3.7 % per year [103, Nexant Inc 2011].

Key environmental issues
The key environmental issue for the production of ethylene oxide and ethylene glycols is the emission to air from the EO section (VOCs and ethylene oxide).

7.2 Applied processes and techniques

7.2.1 Process options

The principal option for the production of ethylene oxide is the direct oxidation of ethylene, and this is the only process described in detail in the subsequent sections of this chapter. It has replaced the chorohydrin route which is also briefly reviewed below.

The principal option for the production of ethylene glycol is the thermal hydrolysis of ethylene oxide, and this is the only process described in detail in the subsequent sections of this chapter. An alternative is the hydrolysis of ethylene carbonate to produce monoethylene glycol (MEG) which is also briefly reviewed below.

7.2.1.1 Production of ethylene oxide

7.2.1.1.1 Direct oxidation of ethylene

Ethylene oxide can be produced commercially by the catalytic direct oxidation of ethylene using air or oxygen. However, the use of air has now been fully superseded by the use of oxygen in the EU-28.

Ethylene oxide (EO) is formed by reacting gaseous ethylene and oxygen over a solid, silver-containing catalyst. The exothermic reaction is carried out at an elevated temperature (200–300 °C) and pressure (15–25 bar) with a residence time of a few seconds. Very small amounts of acetaldehyde (from isomerisation of EO) and formaldehyde may also be produced.

$$C_2H_4 + \tfrac{1}{2}\,O_2 \rightarrow C_2H_4O\ (+105\ kJ/mol)$$

The main side products are carbon dioxide and water, which result from a highly exothermic reaction:

$$C_2H_4 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O\ (+1323\ kJ/mol)$$
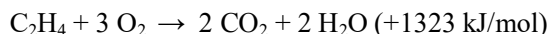
Ethylene oxide may also be oxidised to carbon dioxide and water.

The ratio between the above two reactions defines the selectivity of the process (i.e. the amount of ethylene converted to EO on a molar basis) and is mainly determined by the type of catalyst used. The selectivity to EO is 75–90 % (for the oxygen process) at an ethylene conversion of 8–10 %.

The reaction gases are recycled back to the oxidation reactor once the ethylene oxide product has been removed and there is therefore a need to control the build-up of carbon dioxide produced as a result of the full oxidation of some of the ethylene. Often, carbon dioxide is isolated for beneficial use.

In 2013, the direct oxidation route using oxygen was the only one in use in the EU, and it was anticipated that any new plant would also adopt the use of oxygen rather than air. Therefore it is the only route for the production of ethylene oxide that is considered further in this chapter.

7.2.1.1.2 Chlorohydrin route

This costly, two-stage process involves the liquid-phase reaction between ethylene and hypochlorous acid to form an ethylene chlorohydrin intermediate, followed by conversion to EO with hydrated lime. The EO selectivity is about 80 %. However, this route results in the formation of unwanted ethylene dichloride and calcium chloride. Due to the high cost of

chemical feedstocks (especially chlorine) and the considerable effluent load, this route has been replaced by direct oxidation and is therefore not considered further in this chapter.

7.2.1.2 Production of ethylene glycols

7.2.1.2.1 Thermal hydrolysis of ethylene oxide

At the time of writing (2015), the thermal hydrolysis of ethylene oxide accounts for all of the ethylene glycols manufactured in the EU.

This route involves the following sequence of process steps:

- reaction of ethylene oxide with a significant stoichiometric excess of water at a temperature of 120–250 °C and a pressure above 10–40 bar;
- separation by distillation (and subsequent recycling) of the water from the ethylene glycols mixture;
- separation by distillation of the mono-, di-, tri- and polyethylene glycols, employing progressively higher levels of vacuum.

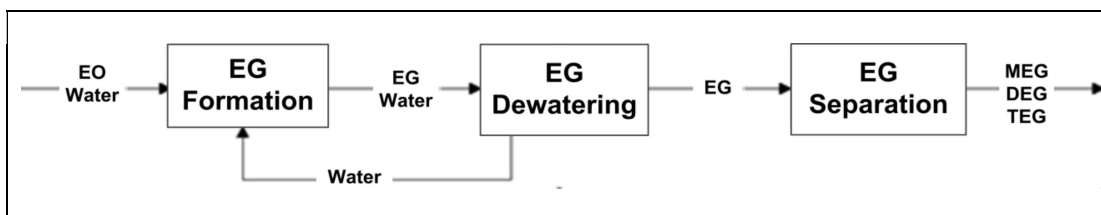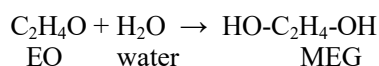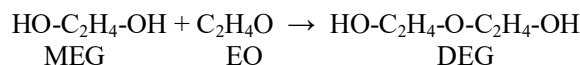The process can be summarised as shown below.

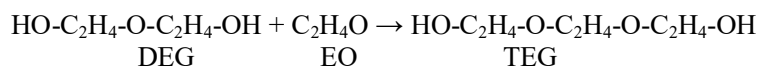**Figure 7.1:   Process flow diagram for ethylene glycol production**

In commercial units, the crude glycols mixture typically contains between 75 wt-% and 92 wt-% monoethylene glycol (MEG).

$$C_2H_4O + H_2O \rightarrow HO\text{-}C_2H_4\text{-}OH$$
$$\text{EO} \qquad \text{water} \qquad\qquad \text{MEG}$$

The main co-product in the MEG manufacturing process is diethylene glycol (DEG), which is formed by the reaction of MEG with EO.

$$HO\text{-}C_2H_4\text{-}OH + C_2H_4O \rightarrow HO\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}OH$$
$$\text{MEG} \qquad\qquad \text{EO} \qquad\qquad \text{DEG}$$

The DEG can react further again with EO (ethoxylation) to form triethylene glycol (TEG) and heavier glycols.

$$HO\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}OH + C_2H_4O \rightarrow HO\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}OH$$
$$\text{DEG} \qquad\qquad\qquad \text{EO} \qquad\qquad \text{TEG}$$

7.2.1.2.2 Hydrolysis of ethylene carbonate

Ethylene oxide can be reacted with carbon dioxide (using the CO_2 evolved from the oxidation of ethylene to ethylene oxide) to produce ethylene carbonate as an intermediate. The subsequent hydrolysis of ethylene carbonate results in the selective production of monoethylene glycol (which is quite often the preferred co-product) and is effectively a variation on the thermal hydrolysis route albeit requiring less water for the reaction.

The process is applied in some new plants outside Europe, e.g. by Lotte Petrochemicals in Daesan, South Korea; by Petro Rabigh, a Saudi Aramco/Sumitomo Chemical joint venture, in Rabigh, Saudi Arabia; and by Shell in Singapore [114, Shell 2009]. From an economic point of view, it may be the preferred route where (unlike in Europe) the market demand for DEG and TEG is low.

At the time of writing (2015), this route is not used in the EU and is therefore not considered further in this chapter.

7.2.2 Direct oxidation route

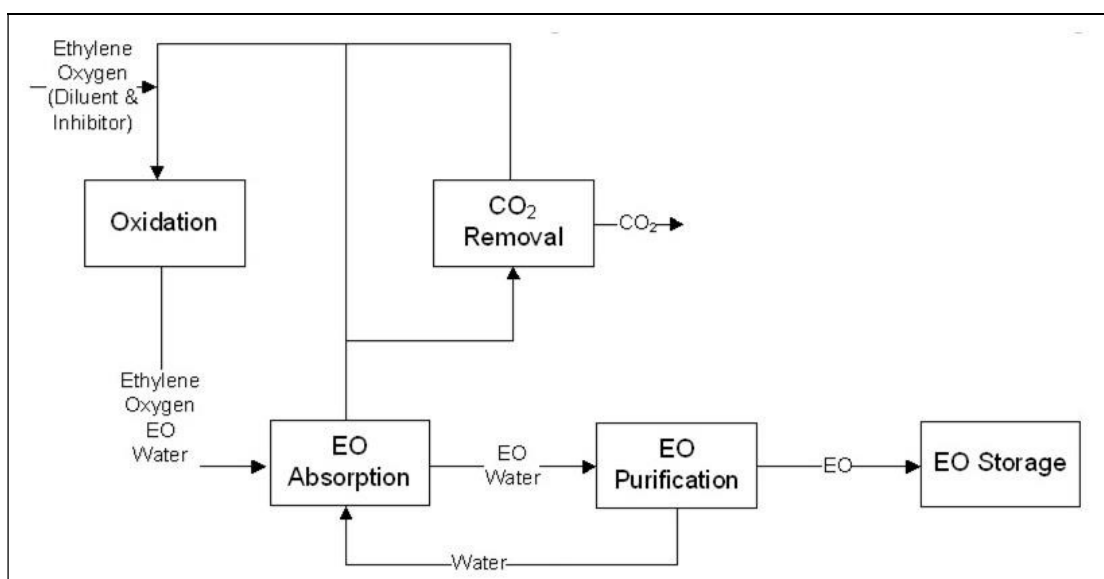The manufacture of ethylene oxide using oxygen is shown in Figure 7.2 below.

Figure 7.2: **Process flow diagram for ethylene oxide production**

EO/EG processes can be designed for the production of:

- glycols only (without high-purity EO recovery);
- high-purity EO only with a minimum production of unavoidable glycols;
- a product mix of high-purity EO and glycols in an integrated plant.

In practice, the third configuration is usually adopted because:

- MEG is the most important outlet for EO;
- the EO process intrinsically forms glycols, which require work-up;

- it provides efficient heat integration of the exothermic EO and energy-consuming EG stages (the reaction of EO and water to make glycols is exothermic but the glycol plant is a net consumer due to the large heat demand of the evaporation and distillation stages).

Although there are a number of different EO/EG manufacturing process licensors, the process technologies are broadly similar and the unit operations can be grouped into four stages:

- Stage 1: EO reaction, EO recovery and carbon dioxide removal;
- Stage 2: non-condensables removal and EO purification;
- Stage 3: glycols reaction and dewatering;
- Stage 4: glycols purification.

These steps are described in detail below.

7.2.2.1 Ethylene oxide reaction (Stage 1.1)

Feedstock ethylene is typically received by pipeline from a steam cracker. The oxygen can be provided by air (in an air-based process) but modern processes are based on pure oxygen supplied by pipeline from an air separation unit. Both the oxygen and the ethylene have to be extremely pure.

The reaction between ethylene and oxygen is carried out in a multi-tubular, fixed-bed type reactor, with a silver catalyst in the tubes and a coolant on the shell side. The heat generated by the exothermic reactions is removed by the coolant and is recovered by producing steam. The steam is used as a heating medium in various sections of the plant.

A large gas flow is circulated continuously through the EO reactors. Reaction products (EO, carbon dioxide and water) are removed from the circulating gas while unconverted oxygen and ethylene are recycled back to the reactor. There is a fire and explosion risk with heterogeneously catalysed direct oxidation processes and the recycle gas therefore contains a diluent which allows operation at oxygen levels that do not create a flammable mixture. All sites that responded to the questionnaire use methane as a diluent which, in comparison to nitrogen, allows for higher oxygen levels, is more effective in limiting temperature rise, requires less energy for the recirculation/compression of the process gases and allows the use of purge gases as fuels. (However, occasionally methane may not be available; in that case, nitrogen would be used for a limited period of time.) A small amount of an organic chlorinated compound (typically ethylchloride or dichloroethane) is added to the recycle gas for catalyst performance control and the chlorine will end up in various product and effluent streams, partly as inorganic chloride (e.g. NaCl).

A vent stream, the inerts purge, is taken from the recycle gas (about 0.1–0.2 vol-%) in order to reduce the build-up of inerts like ethane, argon and nitrogen, and impurities present in the ethylene and oxygen feedstocks. The inerts vent is typically used as fuel gas and burnt (e.g. in a cracker furnace or steam boiler).

Make-up ethylene, oxygen and diluent are added to the recycle gas loop.

Plants that in the past that used air instead of pure oxygen as a feedstock had a slightly different configuration: In order to dispose of the large volume of inert nitrogen that enters the process via the air feed, part of the recycle gas was routed to a second EO reactor (purge-reactor) to convert most of the ethylene. EO was recovered from the purge-reactor product gas via absorption in water, and the remaining gases (unconverted ethylene, nitrogen and carbon dioxide) were vented to atmosphere. When compared with pure oxygen plants, air-based plants had higher atmospheric emissions and lower yields.

7.2.2.2   EO recovery (Stage 1.2)

EO is completely miscible with water. At ambient temperatures and in the absence of catalysts, the reactivity of EO with H_2O (to form glycols) is very low over a wide pH range, which makes water a suitable scrubbing medium for EO removal/recovery. EO is recovered from the gaseous reactor effluent by absorption in water. The aqueous EO solution from the absorber is concentrated in a stripper (desorber). The top stream of the stripper is a concentrated EO-water mixture that is routed to a section for non-condensables removal and EO purification (Stage 2, see below). The bottom stream of the stripper is an EO-free water stream that is cooled and returned to the EO absorber.

Typically one or more bleed streams are taken from the EO recovery section to reduce the accumulation of glycols and/or salts, which are further processed to recover EO and/or glycols.

7.2.2.3   Carbon dioxide removal (Stage 1.3)

Part of the recycle gas that leaves the EO absorber is routed through a column in which carbon dioxide (generated in the oxidation process) is removed by absorption under pressure as hydrogen carbonate in a hot potassium carbonate solution:

$$CO_2 + K_2CO_3 + H_2O \rightarrow 2\ KHCO_3$$
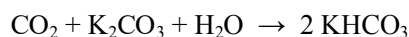
The carbon dioxide is subsequently removed from the carbonate solution in an atmospheric stripper (back reaction). The carbon dioxide vent from the top of the stripper is either routed to atmosphere or recovered for further use (e.g. carbonated drinks), after treatment to remove VOCs. The regenerated carbonate solution from the stripper bottom is cooled and recycled to the carbon dioxide absorber. The carbon-dioxide-depleted overheads stream from the absorber is recombined with the recycle gas stream and routed to the EO reactor(s).

7.2.2.4   Non-condensables removal and EO purification (Stage 2)

The overhead stream of the EO stripper (desorber), an EO-steam mixture, is partially condensed and routed to a purification unit for removing traces of carbon dioxide, ethylene and other non-condensables, e.g. by stripping. The non-condensables are routed back to the recycle gas loop while the purified EO-water mixture is routed to a unit for high-purity EO recovery and/or to the glycols reactor.

Most plants in Europe have an EO purification unit in which high-purity EO is recovered via distillation from the purified EO-water mixture. The remaining process water is either recycled to the EO recovery section or routed to the glycols unit. The EO product is typically chilled and routed to storage.

EO is a gas at ambient temperatures. It is generally stored under a nitrogen blanket below the boiling point (10.8 °C), although it can also be stored at ambient temperatures and elevated pressures. Vent gases from EO storage and other EO-containing vent gases are typically routed to atmosphere via an absorber that recovers the EO and recycles it to the process. If not used immediately on site, EO is normally shipped in railroad tank cars that are loaded directly from plant storage tanks. The transfer generally occurs at about 350 kPa nitrogen pressure.

7.2.2.5   Glycols reaction and dewatering (Stage 3)

Glycols are manufactured by feeding a mixture of EO and water to a reactor that is operated at an elevated temperature (typically 150–250 °C). Under these conditions, reaction rates are fast and no catalyst is required. Sufficient residence time is provided to react all the EO to full

conversion. A reactor pressure of 10–40 barg is typically applied to avoid vaporisation of the EO. The reactor feed contains an excess of water in order to limit the adiabatic temperature rise and to enhance the selectivity to MEG. Typically the glycol products consist of 75–92 wt-% MEG, with the remainder being DEG and some TEG. All (100 %) of the EO feed is converted into glycols (either MEG, DEG, TEG or heavy glycols).

The product stream from the glycols reactor contains the various glycol products and the excess water. The excess water is removed by multiple-effect evaporation with subsequent vacuum distillation and, after heat exchange, is recycled back to the glycols reactor. A bleed is taken from the recycled water to reduce the build-up of impurities. Low-pressure steam generated in this stage is used as a heating medium at various locations in the plant.

7.2.2.6   Glycols purification (Stage 4)

The water-depleted crude glycol stream is fractionated in a number of vacuum columns to recover the individual glycol products at a high purity level. Co-products in the MEG manufacturing process are, in decreasing amounts, diethylene glycol (DEG), triethylene glycol (TEG) and heavier glycols. The individual glycol products are recovered by subsequent fractionation. The glycol products are cooled and routed to storage. The bottom stream from the last vacuum column contains the heavier glycols and can be sold for further glycol recovery or sent for disposal (e.g. incineration).

7.2.3   Other than normal operating conditions

OTNOC operations cover planned and unforeseen events. They may result in higher or lower emissions and affect one or more environmental media. Emissions to the environment will depend on the systems in place to prevent an increase in emissions (e.g. redundancy or back-up systems for key abatement devices) and to prevent unforeseen events (see Section 2.4.11).
The following lists are examples of operations that deviate from the stable and normal operating procedures.

7.2.3.1   Specific other than normal operating conditions

The following operations deviate from the stable and normal operating procedures:

- Product isolation: A problem with the operation of the ethylene oxide scrubber would result in higher quantities of ethylene oxide in the recirculating gases and therefore in the purged gas stream. As ethylene oxide has a high vapour pressure, a problem with incomplete recovery of ethylene oxide from the recycled scrubbing water could also result in an elevated ethylene oxide level in the recirculating gases post-scrubbing.

- Heat removal: The oxidation is exothermic and this heat is normally removed by vaporising water to produce steam (or by heating oil). If the supply of water (or oil) were to be interrupted or reduced to a problematic level, or some other problem occurred that gave rise to the same outcome, this could result in the overheating of the reactor, which could in turn result in a runaway reaction, and therefore a need for the pressure relief system to operate.

- Overdosing: The overdosing of the organochlorine inhibitor would increase the amount of this that is present in the recirculating process gases and therefore the amount that would be present in the purge gas stream.

- Contamination: The presence of a substance that would catalyse the polymerisation of ethylene oxide could result in a runaway reaction that would probably require the operation of emergency relief systems, resulting in a release to the environment.

7.2.3.2 Generic other than normal operating conditions

The following generic events deviate from standard operating procedures in EO manufacturing plants:

- Routine start-up: The process of filling the plant could result in displaced gases that would ultimately need to be vented.
- Shutdown for maintenance preparation: When the plant is shut down its inventory will need to be removed, and a process of purging may be employed in order to eliminate hazardous substances (and ethylene oxide in particular), particularly where maintenance activities are anticipated. This involves equipment flushing, a higher load being sent to the WWT, and potential emissions to the surface water (rainwater) header.
- Malfunction of pressure control: A problem with a storage tank's pressure control system (possibly the nitrogen supply valve or a terminal PSV) could result in ongoing emissions. This could be a particular issue where pressurised nitrogen filling operations are practised.
- Malfunction of temperature control: A problem with the supply of chilled cooling service (due to a stuck valve, pump failure, control loop issue, etc.) could lead to 'boiling' and therefore an over-pressurisation that might lead to an emission.
- Malfunction of abatement: A problem with any scrubber or oxidiser whose duty it is to abate emissions from storage.
- Air leakage greater than normal into systems that operate under vacuum: This will increase the ejector water/steam usage, and net emissions to water or air.
- Plant idle due to loss of containment caused by corrosion or operation of a rupture disc.
- Service or utility failure: Malfunction of cooling water and/or chilled water, power, distributed control system (DCS), or instrument air.

7.2.4 Equipment important for environmental protection

The following systems perform important operations for environmental protection and require the longest uptime possible:

- air:
    - vent gas treatment (scrubbers, oxidisers);
    - recycled gas control in oxidation loop;
    - CO_2 removal/treatment system;
- water:
    - stripping;
- waste:
    - catalyst management system/procedures.

7.3   Current emission and consumption levels

If not stated differently, the emission and consumption data in this chapter for the production of ethylene oxide refer to the oxygen-based process using methane as a diluent. In some places, information for the former air-based process is included mainly in order to illustrate the environmental benefits of the oxygen-based route.

The main sources of emissions to air and water are shown in Figure 7.3 for the EO plant and in Figure 7.4 for the EG unit.
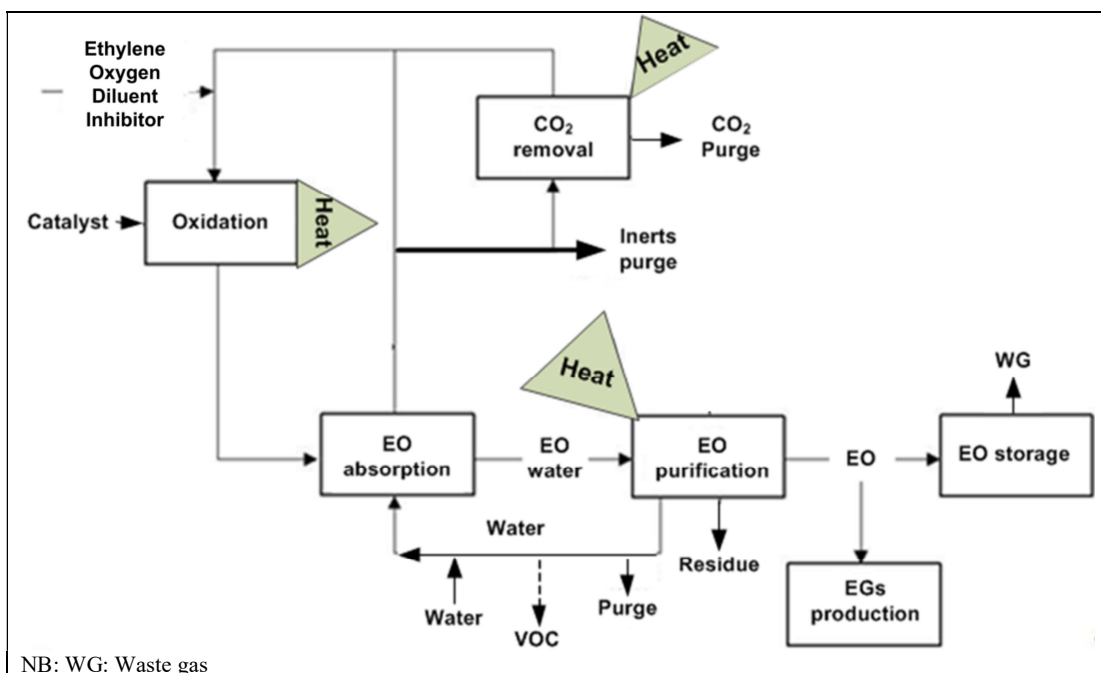

NB: WG: Waste gas

Figure 7.3:   Block flow diagram of an EO plant and its emission sources
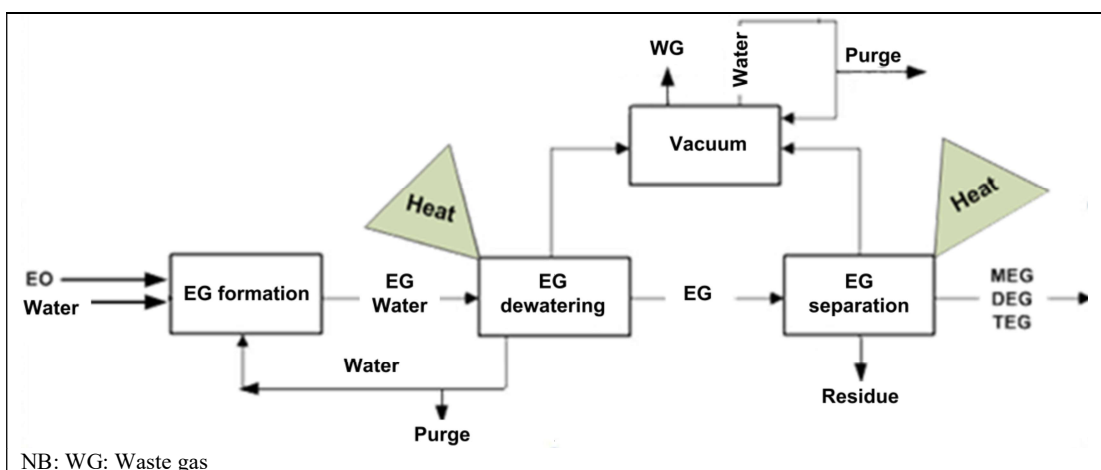

NB: WG: Waste gas

Figure 7.4:   Block flow diagram of an EG plant and its emission sources

7.3.1 Emissions to air

A rather dated report [130, EC VOC Task Force 1990] gives average VOC arisings (prior to treatment) from ethylene oxide plants as 20.5 kg/t of ethylene oxide product. In air-based plants VOCs mainly arise from the secondary absorber vent and the fractionating tower vent, whilst in oxygen-based plants the main sources are the vent gas scrubber and the carbon dioxide absorption system. A comparison of VOC arisings is given in the table below.

Table 7.2:   Specific emissions to air from EO production

	Air-based plants	Oxygen-based plants
Methane (kg/t of EO product)	6	3
Ethylene (kg/t of EO product)	92	0.1–2.5
Ethylene oxide (kg/t of EO product)	1	0.5

7.3.1.1 Inerts purge from the reaction section

Contrary to the air-based process where the inerts purged from the gas loop form a large stream, the inerts purge from the oxygen-based process is only a small part of the recycled gas (e.g. 0.1–0.2 %) and consists mainly of hydrocarbons (e.g. methane, ethane) as well as some argon and nitrogen. Small amounts of ethylene dichloride or ethyl chloride, which are used in small quantities to modify the oxidation reaction, are also present. This stream is passed to the fuel gas network for combustion.

The purge can be located upstream (as shown in Figure 7.3) or downstream of the CO_2 removal step. According to the data collection, approximately half of the installations have the purge upstream of the CO_2 removal and half downstream.

The composition of the inerts purge is as follows:

- Some of the carbon dioxide that results from the full oxidation of a portion of the ethylene will be present irrespective of whether the purge occurs before or after the CO_2 removal step. Due to the desire to target selectivity rather than per pass conversion efficiency, the recirculating process gas will also contain significant unreacted/unoxidised ethylene, and there will also be unreacted oxygen present. The relative proportions of ethylene, oxygen and carbon dioxide will depend on the addition rates of the reagents, the conversion rate and selectivity of the oxidation reaction, and the location at which the purge stream is removed.

- The recirculating process gas, and therefore the purged gas, still contains some traces of ethylene oxide.

- The addition of an organochlorine inhibitor (such as ethylchloride or dichloroethane) to help minimise the proportion of ethylene that is fully oxidised to carbon dioxide will mean that this too will be present in the recirculating gases (no more than trace levels).

- A diluent, normally methane, will normally be added to allow the process to operate safely at a higher oxygen concentration. According to the data collection, under normal operating conditions all installations use methane as a diluent.

- Contaminants present in the raw materials (e.g. ethane and argon) and by-products formed within the process (e.g. acetaldehyde, formaldehyde, acetic acid and formic acid) will also be present at generally very low levels in the purge gas stream, although some of these (and also some ethylene) will be absorbed to a certain extent during the ethylene

oxide scrubbing step, and may ultimately form part of the light ends [40, US EPA 1986], [42, Reuss et al. 2012], [90, Rebsdat et al. 2012].

7.3.1.2 Emissions to air from the CO_2 removal section

A portion of the ethylene is fully oxidised to carbon dioxide, and some of this therefore needs to be removed from the recirculating process gas stream in order to maintain the CO_2 concentration at an appropriate level. Carbon dioxide is removed from the recirculating process gases by absorbing an appropriate proportion of the recycled process gas after ethylene oxide isolation into an appropriate medium (normally potassium carbonate), from which the carbon dioxide can subsequently be desorbed by stripping.

In the oxygen-based process, the overhead stream of the carbon dioxide stripper (shown as the CO_2 purge in Figure 7.3) contains carbon dioxide, water (steam) and small amounts of ethylene, methane, EO and aldehydes. It can be treated by thermal or catalytic oxidation. The resulting stream is essentially pure carbon dioxide (and water) containing traces of hydrocarbons (methane and/or ethylene). Where possible, it is sold to a customer. More often, the treated stream is vented to atmosphere. Specific emission levels are given in Table 7.3.

Table 7.3: Specific emissions to air from EO processes

	Before treatment		After treatment	
	All units	**Lowest 50 %**	**All units**	**Lowest 50 %**
Ethylene (kg/t of EO ex reactor)	0.1–2	NI	NI	NI
Methane (kg/t of EO ex reactor)	0–1	NI	NI	NI
Ethylene and methane (kg/t of EO ex reactor)	0.4–3	0.4–1	0*–3.1	0*–0.2
* In the case of treatment by catalytic/thermal oxidation, the emissions are considered to be zero. NB: NI No information provided. *Source:* [41, CEFIC 2010]				

The following ranges have been derived (for the oxygen-based process) from the questionnaires.

Table 7.4: Specific emissions to air from the CO_2 purge of the EO processes

	Without/before final treatment		After catalytic oxidation	
	No of installations	**Emission (kg/t of EO ex reactor)**	**No of installations**	**Emission * (g/t of EO ex reactor)**
Methane	3	0.03–1.45	3	0.2–8
NMVOC	3	0.07–1.35	3	0.8–9
* Including installations where the CO_2 stream is marketed instead.				

The reported common methods for monitoring these streams are as follows.

Table 7.5: Monitoring methods for emissions to air

Analytical method	NMVOC	Methane	Aldehydes
	DIN EN 13649 GC, GC/MS, HPLC	ISO 14965 EN GC	DIN EN 13649 GC/MS, HPLC
Frequency	Once a year	Once a year	Once a year
Sample size	1 000 cm^3	1 000 cm^3	1 000 cm^3
Reference	Dried CO$_2$	Dried CO$_2$	Dried CO$_2$

7.3.1.3 Emission of VOCs to air from EO isolation

The water into which the ethylene oxide is absorbed will also contain some of the various VOCs that are present in the recirculating process gas (e.g. ethylene, aldehydes, organochlorine inhibitor), and these are stripped from the desorbed ethylene oxide prior to its purification. The overheads from the column are also likely to contain some ethylene oxide. If they are not recycled to the process, the fact that they may contain ethylene oxide and other VOCs means that they would need to undergo appropriate treatment before release.

7.3.1.4 Emissions of EO to air from scrubbers

The common treatment system for EO-containing vent streams, e.g. from EO recovery/purification, is a wet scrubber that recovers EO. It has an overhead stream of nitrogen that contains some EO. If no further VOC abatement is required, this scrubber outlet stream is vented to atmosphere. The range of EO concentrations for all units is 0.1–40 ppm wt (around 0.13–54 mg/Nm^3), and the lowest 50 % of units contain 0.1–3 ppm wt (around 0.13–4 mg/Nm^3) [116, CEFIC 2000], [90, Rebsdat et al. 2012], [41, CEFIC 2010].

7.3.1.5 Emissions to air from EG fractionation

Non-condensable gases are vented from the vacuum system(s) serving the evaporators and distillation columns that are employed to respectively dewater and separate the individual ethylene glycols.

The substances present in the evacuated gases may include:

- ethylene glycols: these have very low vapour pressures and are unlikely to be emitted in material quantities where efficient condensation is employed;
- VOCs: any light ends (volatile aldehyde by-products that are produced during the hydrolysis step and any unreacted ethylene oxide) should be recycled with the water.

7.3.1.6 Emissions to air from open cooling of the EO absorbent

The aqueous bottom stream of the EO stripper (desorber) (see Section 7.2.2.2) needs to be cooled before being returned to the EO absorber in order to maintain scrubbing efficiency.

While most plants use indirect cooling, in some plants the water used to absorb EO is cooled down in a cooling tower. As this water contains some traces of organics, the air from the cooling tower contains VOCs. There is no direct treatment of the gas stream leaving the cooling tower and cooling tower vapours are vented to atmosphere. VOC emissions are instead reduced by improving the stripping at the EO stripper. The final emission to atmosphere is usually less than 0.03 kg VOC/t of EO ex reactor) (compared to emissions of up to 0.6 kg VOC/t of EO ex reactor without optimisation of the stripping [116, CEFIC 2000]). However, this emission

quantification is difficult because the VOC content in the air stream is close to, or even below, the limit of detection, and the organics content in the absorbing water shows only little variation from the inlet to the outlet of the cooling tower.

7.3.2 Emissions to water

The aqueous effluent streams are typically treated biologically in central facilities together with other streams (see the CWW BREF) and this makes it difficult to establish the true contribution to the overall emissions. Discontinuous waste water streams are also present. The rinsing of process equipment, for example prior to maintenance, creates a weak stream of hydrocarbons. The number of cleaning operations is highly dependent on the maintenance regime and the frequency of discharge may range from 10 times per year to once every five years.

7.3.2.1 Effluents from EO production

The absorption of the ethylene oxide product in water will result in the inevitable formation of some ethylene glycols. As the absorption water is recycled, there is a likelihood of a build-up of ethylene glycols, and a purge stream (as shown in Figure 7.3) is consequently needed in order to limit the extent of this. Furthermore, there is potential for salts to also build up within this recycle loop.

The need for the purge stream is primarily to manage ethylene glycol levels, so ethylene glycols will therefore be present. The purge stream may also contain organic acids or their salts if the pH is adjusted.

The purge stream is removed after the concentration of the ethylene oxide prior to its purification. The purge stream should therefore contain only trace amounts of ethylene oxide under normal operating conditions.

The purge stream is usually concentrated at the EO unit (to attain marketable by-products) or routed to the EG unit for reuse and further processing. When the concentration of organics is too low for recovery and the purge stream does not meet the quality demands for reuse in an associated EG plant, it is discharged as waste water and routed to biological treatment.

7.3.2.2 Effluents from EG production

In order to maximise the formation of monoethylene glycol, a significant stoichiometric excess of water is normally used during the ethylene oxide hydrolysis reaction. Both the amount of effluent that is generated and the quantity of water that is consumed are minimised by recycling the water after it has been separated from the ethylene glycols. Aldehydes that are formed during the hydrolysis reaction will remain in the water and their levels therefore need to be controlled by purging some of the recycled water (see Figure 7.4). It is possible that this purge may be disposed of as an effluent. It will contain aldehydes and possibly ethylene glycols.

7.3.2.3 Emissions to water from vacuum systems

The separation of the individual ethylene glycols is achieved by multiple distillations that are conducted under vacuum conditions. The systems employed for generating the vacuum can comprise steam ejectors and/or liquid ring pumps, in which case an aqueous effluent may arise. As ethylene glycols are readily condensable (due to their low vapour pressures) and miscible with water, any that are present (i.e. uncondensed or entrained) in the evacuated gases are likely to be mainly transferred to any effluents that might arise from the vacuum systems, either

condensate from steam ejectors or water purges from liquid ring pumps that use water (rather than glycol) as a sealing liquid.

7.3.3 Raw material consumption

7.3.3.1 Consumption of ethylene and oxygen

EO/EG production has two main raw materials, ethylene and oxygen (or formerly air). Typical ranges are given in Table 7.6.

Table 7.6: Raw material consumption of ethylene oxide processes

		Oxygen-based process	Air-based process
Ethylene	Selectivity (%)	75–90	65–75
	Consumption (kg/t of EO ex reactor)	700–850	800–900
Oxygen	Consumption (kg/t of EO ex reactor)	600–1 100	
Source: [116, CEFIC 2000] revised by CEFIC in 2014			

The raw material consumption and the energy consumption depend on the selectivity of the EO catalyst (see Section 7.4.3.1.1).

7.3.3.2 EO consumption at EG plants

The various co-products (mono-, di- and triethylene glycols) all have potential uses and values, and the ethylene oxide consumption therefore has to be seen in the context of the desired (or at least accepted) co-product profile.

The main reason for an increased ethylene oxide consumption rate per tonne of target product could be loss of material in the bottom product from the final separation column.

The loss of ethylene glycols in the purge from the water stream being recycled back to the glycol reactor will also result in an increase in the ethylene oxide consumption rate.

7.3.3.3 Other consumption at EO plants

Other consumption at EO plants includes the use of methane as a diluent, of an organochlorine inhibitor (such as ethylchloride or dichloroethane) and of potassium carbonate for the absorption of CO_2.

7.3.4 Energy consumption

The EO/EG process is both a consumer and a producer of energy:

- The EO reaction section is typically a net energy producer and this is used to generate steam. The steam production depends on the EO catalyst selectivity, which in turn depends on the type and age of the catalyst.
- The EG section is a net consumer of energy. A multi-effect evaporator system can be used in the glycols dewatering section to reduce energy consumption. Furthermore, the

heat released in the glycols reactor is used to reduce the energy consumption of the glycols dewatering section.

Catalyst selectivity and the relative sizes of the EO and EG sections influence the overall energy balance of the unit and define whether a plant is a net steam importer or exporter. Low catalyst selectivity (and therefore increased oxidation of ethylene to carbon dioxide) gives a higher level of reaction heat release and steam generation in the EO reaction section.

Apart from generating steam, the process also generates a number of gaseous and liquid effluent streams that may be recovered as fuel for furnaces, power plants or steam boilers. Optimisation of the energy balance is therefore typically on a site-integrated basis. Since each European plant has different characteristics, it is difficult to give a meaningful range of energy consumption figures. Even when they are available, care is required in interpretation as lower energy consumption could mean that a plant is converting more ethylene into carbon dioxide.

Fractionation operations

Energy is required for the removal of water from the ethylene glycols reaction mixture and the subsequent fractionation of the individual ethylene glycols which require an evaporation step followed by a series of distillations.

Vacuum generation

The separation of the individual ethylene glycols is achieved by distillation columns in series operating under vacuum. Vacuum generation options include liquid ring pumps and/or steam ejectors. Given the progressively high boiling points of the ethylene glycols, the level of vacuum is likely to be high, and this is likely to translate into a relatively high energy demand.

Gas recycling

The pursuit of selectivity rather than rate of conversion means that a significant proportion of the process gases need to be recirculated back to the reactor. This will require the operation of compressors and these will have a potentially significant energy demand.

7.3.5   Water usage

EO production

Water is used within the process to absorb ethylene oxide. The ethylene oxide is separated from the water later in the process and this allows the recycling of the water (after suitable cooling). Additional water is required to compensate for the purge stream from the recycled water that is necessary in order to limit the build-up of glycols that are formed during the absorption.

The net water usage may be marginally affected by the water that will arise as a consequence of the full oxidation of ethylene.

EG production

As ethylene glycols are produced via a hydrolysis reaction, there is a net consumption of water by the process due to the chemical reaction. However, in order to limit the formation of heavy glycols, a significant stoichiometric excess of water is normally used which is usually recycled after it has been evaporated from the ethylene glycols mixture.

The main reason for requiring additional water over and above that which has reacted will therefore be to compensate for the purge stream from the recycled water that is necessary to limit the build-up of aldehydes that are formed during the reaction.

7.3.6 Co-products, by-products and waste generation

7.3.6.1 Carbon dioxide

As explained in the process description (Section 7.2.2), carbon dioxide is the main by-product of the direct oxidation. A selectivity of 70–90 % would correspond to a maximal ratio of 0.86–0.22 tonnes of CO_2 per tonne of EO produced in the reaction.

The stream is purified and either liquefied by a downstream unit for marketing or released to atmosphere.

7.3.6.2 Glycol residue from the EO recovery and purification

A residue arises during the purification of ethylene oxide. Any stream with a high concentration of hydrocarbons is usually sold as a by-product (optionally after further processing in the EG plant) or otherwise incinerated as a waste. In the 2003 LVOC BREF, the rate of arisings was reported to be in the range of 0.5–10 kg/t of EO ex reactor, and the typical hydrocarbon content was 40 wt-% TOC [116, CEFIC 2000]. The data collection showed higher values for glycol residue from EO purification, ranging from 3 kg/t to 45 kg/t of EO.

7.3.6.3 EO spent catalyst

The selectivity of the catalyst will deteriorate over time, until it needs to be replaced with fresh catalyst. The EO catalyst loses its efficiency over time and it is periodically changed (typically every one to four years). The rate of generation is 0.12–0.8 kg/t of EO (0.12–0.3 kg/t of EO for the lowest 50 % of units) [116, CEFIC 2000]. The catalyst is sent to reclaimers for recovery of the silver content. The inert, inorganic support for the catalyst requires landfilling once the silver has been recovered.

7.3.6.4 Purge streams and heavies from EG fractionation and purification

The EG fractionation and purification result in some purge streams being generated along with a bottom stream of heavy glycols (oligomers) from the last column of the glycols separation unit. If customers can be found, the stream is usually sold. Alternatively it may be incinerated. The data collection shows residues from EG separation ranging from 1.4 kg/t to 21 kg/t of EO, including the cases in which the purge stream from the EO plant is routed to the EG plant.

7.4 Techniques to consider in the determination of BAT

This section describes techniques (or combinations thereof), and associated monitoring, considered to have the potential for achieving a high level of environmental protection in the activities within the scope of this chapter. The techniques described will include both the technology used and the way in which the installations are designed, built, maintained, operated and decommissioned.

It covers process-integrated techniques and end-of-pipe measures. Waste prevention and management, including waste minimisation and recycling procedures are also considered, as well as techniques that reduce the consumption of raw materials, water and energy by optimising use and reuse. The techniques described also cover measures used to prevent or to limit the environmental consequences of accidents and incidents, as well as site remediation measures. They also cover measures taken to prevent or reduce emissions under other than normal operating conditions (such as start-up and shutdown operations, leaks, malfunctions, momentary stoppages and the definitive cessation of operations). Cross references to other chapters are used, where relevant to avoid repetition.

Annex III to the Directive lists a number of criteria for determining BAT, and the information within this chapter will address these considerations. As far as possible, the standard structure in Table 2.6 is used to outline the information on each technique, to enable a comparison of techniques and the assessment against the definition of BAT in the Directive.

This chapter does not necessarily provide an exhaustive list of techniques which could be applied. Other techniques may exist, or may be developed, which could be considered in the determination of BAT for an individual installation.

7.4.1 Techniques to reduce emissions to air

7.4.1.1 Process route selection: Use of oxygen instead of air

Description
Ethylene oxide production process based on oxygen feed instead of air.

Technical description
The oxidation reaction to produce ethylene oxide is carried out with oxygen instead of air to improve process efficiency (by increased selectivity). Methane is used as a diluent (instead of nitrogen) which allows the inerts purge to be used as a fuel gas.

Achieved environmental benefits
- Lower ethylene consumption, lower carbon dioxide formation and less off-gas.
- Allows the recovery of pure carbon dioxide which can be reused (e.g. for blanketing or sale).
- Lower emissions to air.
- Lower energy consumption.

Environmental performance and operational data
The selectivity and consumption ranges of the oxygen-based process are listed in
Table 7.6 in Section 7.3.3.1, including the improvements in comparison to the air-based process.

Cross-media effects
The oxygen-based process requires pure oxygen as a feedstock, and energy is used in the manufacturing of the oxygen. Improved selectivity implies less heat formation/recovery (see Section 7.3.4).

Technical considerations relevant to applicability
This technique is applicable to new installations or major retrofits.

Economics
The additional costs of pure oxygen consumption are more than compensated by the reduced ethylene use and lower capital requirements per tonne of product. Costs for VOC abatement are also reduced.

Driving force for implementation
Economics.

Example plants
The first generation of EU plants used air but they have been replaced by, or converted into, plants using pure oxygen. EO plants in the EU now all use pure oxygen feed.

Reference literature
No reference literature provided.

7.4.1.2 Techniques to reduce VOC emissions from the reaction section

According to the data collection, all installations use the inerts purge as fuel gas. Most installations in the EU recover ethylene from the inerts purge beforehand, either via PSA (adsorption) or membrane separation.

7.4.1.2.1 Recovery of ethylene

Pressure-swing adsorption (PSA) is a separation method in which gas molecules are retained on a solid or liquid surface (adsorbent, also referred to as a molecular sieve) that prefers specific compounds to others and thus removes them from effluent streams. See the CWW BREF for further information.

Membrane separation is used to concentrate the organic content for recovery. See the CWW BREF for further information.

7.4.1.2.2 Routing of the inerts purge to a combustion unit

This technique involves the recovery of energy by reusing the stream as fuel, e.g. in site boilers. See the LCP BREF for a technical description.

7.4.1.3 Techniques to reduce emissions from the CO_2 removal system

Carbon dioxide is removed by absorption in a hot carbonate solution. Carbon dioxide is then stripped from the carbonate solution by means of lower pressure and heat. The vent stream is mainly composed of carbon dioxide and water, but also contains VOCs (mainly ethylene and methane).

The carbon dioxide stream is reduced by any technique that improves the selectivity of the oxidation reaction (see Section 7.4.3.1).

7.4.1.3.1   Recovery of the carbon dioxide for sale as a product

As the carbon dioxide is normally isolated in a relatively pure form, it can be used beneficially, typically after further treatment, e.g. by catalytic oxidation (see Section 7.4.1.3.3), in order to remove VOCs.

The beneficial use of CO_2 will reduce the CO_2 emissions to air from the installation. The feasibility will depend on the market situation and the availability of third-party investors to build a CO_2 recovery plant.

On a life-cycle basis, the achieved reduction of CO_2 emissions will depend on the way CO_2 is used (e.g. for soft drinks) and the alternative CO_2 sources for this use.

In the answers to the questionnaires, about 40 % of the sites reported that the CO_2 stream is marketed.

7.4.1.3.2   Staged carbon dioxide desorption

Description
Recovery of ethylene and methane from the carbonate solution before stripping out the carbon dioxide.

Technical description
Conducting the depressurisation necessary to liberate the carbon dioxide from the absorption medium in two steps rather than one results in the separation of two streams: the main VOC stream from the main CO_2 stream.

'Flashers' can recover a significant amount of the absorbed ethylene and methane from the carbonate solution prior to carbon dioxide removal in the carbon dioxide stripper. The overheads of the flasher can be recycled back to the process.

Achieved environmental benefits
- Lower emissions to air.
- Recovery of material.

Technical considerations relevant to applicability
Applicable to oxygen-based oxidation processes.

7.4.1.3.3   Use of oxidisers for end-of-pipe treatment

The off-gas from the CO_2 stripper consists mainly of CO_2 with VOCs (e.g. ethylene and methane) as pollutants. To achieve low levels of VOCs, it can be treated either with catalytic or thermal oxidisers, to reduce emissions to air or enable reuse of the purified carbon dioxide.

Catalytic oxidiser
See the description in the CWW BREF.

- This is used at at least four sites, according to the data collection; three of those sites are: Sasol, Marl (DE), IQA, Tarragona (ES) and Clariant, Gendorf (DE). It is used to purify the carbon dioxide for reuse/marketing or as final abatement before release to atmosphere.
- After catalytic oxidation, one site reported a load of 0.8 g NMVOC and 0.2 g methane per tonne of EO (from one periodic measurement); others reported NMVOC loads of 4–9 g/t

and 8–9 g/t of EO, and methane loads of 6–8 g/t and 1.3–1.9 g/t of EO from yearly and monthly measurements respectively.

Thermal oxidiser
See the description in the CWW BREF.

This is only used in one of the installations that participated in the data collection – Ineos Oxide, Antwerp (BE).

7.4.1.4   Techniques to reduce emissions to air from EO isolation

The techniques that can be employed to reduce VOC emissions associated with the light end fraction under normal operating conditions include the following:

Gas recompression to recover energy or feedstock
- Recycling of light ends: the light overheads mentioned in Section 7.3.1.3 can be collected and returned to the oxidation reactor loop after recompression. This will involve the recycling of non-condensables, but the features built into the management of the recirculation loop should be able to deal with this. The energy involved in recompression is not anticipated to be high.

Thermal oxidation
- See the CWW BREF.
- For safety reasons, the raw gas should not contain high concentrations of EO, which can be removed beforehand by wet scrubbing.

Catalytic oxidation
- See the CWW BREF.

7.4.1.5   Removal of EO to enable recovery of VOCs and to reduce EO emissions to air

Wet scrubbing is used to remove EO from process streams (to enable VOC recovery/reuse) and from waste gas streams (to abate EO emissions and, for safety reasons, before final treatment in oxidisers).

Scrubbing of process gas streams
Most of the individual process vent streams contain valuable components (ethylene, methane) in addition to EO. The streams are usually routed to a scrubber that is operated at the lowest possible pressure so that all process vents can be routed to it. EO is recovered by absorption in water and recycled back to the process. The scrubber overheads stream is compressed and also recycled back to the process, leaving no residual effluent stream or emission to atmosphere.

Scrubbing of waste gas streams
EO-containing vent streams (e.g. from the process or from storage) that are unattractive for recycling back to the process are typically treated by wet scrubbing. Where the plant configuration allows, the recovered EO solution can be recycled back to the process. If no EO recovery is foreseen, scrubbing may possibly be enforced by adding caustic or acid to enhance the reaction of EO to glycol. The spent scrubbing liquid is then sent to biological treatment.

Depending on the VOC content, the treated waste gas will be routed to further treatment (thermal or catalytic oxidiser).

7.4.1.6 Prevention of fugitive emissions

Due to its toxic and carcinogenic nature, threshold limit values for EO in ambient air are very low (in the order of 1 ppm). For occupational health reasons, extensive measures have been taken by the industry to prevent EO releases, including fugitive emissions, or to detect them at an early stage so that remedial measures can be taken promptly.

In addition to the generic techniques described in Chapter 2, the specific techniques to minimise fugitive emissions may include the following:

Prevention techniques for diffuse emissions of VOCs
- Careful material selection for seals, O-rings, gaskets, etc. in EO duty.
- Use of double seals or tandem seals on pumps in EO duty or use of canned or magnetic drive pumps.

High-integrity equipment
- High-integrity equipment includes: valves with double packing seals; magnetically driven pumps/compressors/agitators; pumps/compressors/agitators fitted with mechanical seals instead of packing; and high-integrity gaskets (such as spiral wound or ring joint) for critical applications.
- As the ethylene glycols separation is carried out under vacuum, reducing leaks (which are not considered an other than normal operating condition in this context) will reduce the quantity of non-condensable gases that enter the distillation plant, thereby reducing the gas volumes handled by the associated vacuum systems, and consequently the likely emissions from them. However, a significant amount of air ingress might affect the level of vacuum that is achieved, which could affect the nature of the process vapours, and may result in a plant shutdown.

Targeted monitoring of pollutants in ambient air (for health and safety)
- Application of metal strips around flanges, with a vent pipe sticking out of the insulation that is monitored for EO release on a regular basis.
- Installation of sensitive EO detection systems for continuous monitoring of ambient air quality (these systems also detect ethylene).
- Monitoring of EO plant personnel for EO exposure (as exposure means emission).

[94, CEFIC 2000], [95, Swedish EPA 2000].

7.4.1.7 Techniques to prevent or reduce VOC emissions from cooling of the EO absorbent

Emissions from open cooling of the EO absorbent as part of the EO absorption-desorption cycle can be reduced by control of the VOC content or preferably prevented by indirect cooling of the absorbent with heat exchangers.

7.4.1.7.1 Complete EO removal by stripping

Description
Emissions are controlled by stripping upstream of the open cooling system, to ensure that no EO is left and to reduce other VOCs.

Technical description
The technique involves maintaining appropriate operating conditions and using online monitoring of the EO stripper operation to ensure that all EO is stripped out; and providing adequate protection systems to avoid EO emissions during other than normal operating conditions.

Achieved environmental benefits
Lower emissions to air of EO and other VOCs.

Environmental performance and operational data
Reduction of VOC emissions to below 0.03 kg/t of EO ex reactor (see Section 7.3.1.6).

Cross-media effects
No information provided.

Technical considerations relevant to applicability
Applicable where cooling is carried out in open cooling towers.

Economics
No information provided.

Driving force for implementation
No information provided.

Example plants
According to CEFIC, 2 out of 11 plants use open cooling systems for the EO absorbent. Both of them use extensive stripping to reduce EO/VOCs.

Reference literature
No reference literature provided.

7.4.1.7.2 Indirect cooling

Description
Use of indirect cooling of the EO absorbent instead of open cooling systems.

Technical description
Indirect cooling is carried out in a closed system with heat exchangers and a separate cooling medium (in this case, cooling water).

Achieved environmental benefits
No VOC emissions to air from the cooling system.

Environmental performance and operational data
No information provided.

Cross-media effects
No information provided.

Technical considerations relevant to applicability
The use of indirect cooling systems to decrease the temperature of liquids is a standard operation in the chemical industry (whereas open cooling systems for process liquids tend to be an exception). For closed cooling circuits, i.e. if the cooling water is recycled, coolers such as cooling towers need to be integrated or, for existing systems on site, adapted to the additional duty.

Economics
Replacing open EO cooling systems with indirect cooling is assumed to be a major investment.

Driving force for implementation
Environmental legislation.

Example plants
According to CEFIC, 9 out of 11 plants use indirect cooling for the EO absorbent.

Reference literature
No reference literature provided.

7.4.1.8 Storage

As a safety precaution, ethylene and oxygen are usually stored outside the EO/EG units and are fed by pipe to the process unit. See the EFS BREF.

Pressure vessels are under a nitrogen blanket and may be refrigerated.

- EO is typically stored in pressure vessels. The nitrogen serves as a diluent in order to keep the vapour phase outside the explosive area. An important issue is avoiding the ingress of air, which could form an explosive vapour mixture with EO, or of other impurities that are reactive with EO or that could catalyse EO runaway reactions.
- EG and heavier glycols are stored in atmospheric vessels because glycols have a lower vapour pressure and emissions to air are negligible.

EO tank vents and purge vents from loading operations are typically routed to a water scrubber that ensures nearly 100 % EO recovery (see Section 7.4.1.5).

7.4.2 Techniques to reduce emissions to water

This document addresses only effluent treatment at source and specific pretreatments. Most EO plants have a collective effluent header that is sent to a waste water treatment unit.

7.4.2.1 Techniques to reduce effluent from EO production

7.4.2.1.1 Use of the purge from the EO unit in the EG unit

Description
Use of the aqueous purge streams from the EO unit in the EG unit.

Technical description
The purge streams from the EO plant are sent to the ethylene glycols process (which has a continuous net water demand) and not discharged as waste water. The extent to which the purge can be reused in the EG process depends on EG product quality considerations.

Achieved environmental benefits
Reduction of emissions to water.

Environmental performance and operational data
No information provided.

Cross-media effects
Depending on the water balance, energy may be required for the removal of additional water from the recovered water/glycol stream.

Technical considerations relevant to applicability
This option is obviously dependent on ethylene glycol production being co-located with ethylene oxide production.

Quality considerations could impose constraints on the application of the technique if the purge stream contains impurities that may affect the quality of the final products. Depending on the plant (and its original design), it may not be possible to recycle this stream as the final products (such as high-purity MEG) would be off spec or of poor quality, making them impossible to sell.

Economics
Depending on the water balance, the benefits from recovery of glycols and reuse of water may be reduced by the operating costs for the removal of additional water from the recovered water/glycol stream.

Driving force for implementation
Economics.

Example plants
Some EU operators reported using this technique in the data collection.

Reference literature
No reference literature provided.

7.4.2.1.2 Distillation of aqueous streams

Technical description
Purge streams from the EO unit and the EG fractionation with high glycol contents can be routed to a distillation or evaporation unit which may be inside the glycol plant or a dedicated unit for the recovery of (most of) the glycols and (partial) recycling of water back to the process.

The technique is used in EO and EG units to concentrate aqueous streams to recover glycols or enable their disposal (e.g. by incineration) and to enable the (partial) reuse/recycling of water.

Achieved environmental benefits
* Reduction of emissions to water.
* Improved resource efficiency (recovery of product, reuse of water).

Environmental performance and operational data
No information provided.

Cross-media effects
Energy consumption of distillation (but reduced energy consumption at the waste water treatment plant and for waste incineration).

Technical considerations relevant to applicability
Regarding waste water management, the technique is used to avoid the discharge of high loads of TOC/COD to the biological treatment plant. At low concentrations, glycols are readily biodegradable.

Depending on the design of the EO plant, the implementation of the technique at an existing EO plant may imply a major revamp and investment, and a potentially lower performance in terms of energy efficiency and product quality.

Economics
Benefits from reduced costs for disposal (waste water, waste) and from recovered glycols (which however may have a comparatively low quality/value).

Driving force for implementation
Economics.

Example plants
Some EU operators reported using this technique in the data collection.

Reference literature
No reference literature provided.

7.4.3 Techniques to reduce raw material consumption

The main raw materials used in the EO/EG process are ethylene and oxygen.

7.4.3.1 Techniques to reduce ethylene consumption

The techniques that can be employed to reduce the specific ethylene consumption due to carbon dioxide formation under normal operating conditions include the following.

7.4.3.1.1 Catalyst selection

By far the most important factor causing raw material consumption to be higher than stoichiometric consumption is the limited selectivity of the EO catalyst. Significant progress has been made to improve catalyst performance, reducing raw material losses by more than 50 %, and further efforts are continuing, mainly driven by economic factors.

A lack of catalyst selectivity will result in a greater proportion of the ethylene being oxidised to carbon dioxide, thereby reducing the proportion of ethylene that is converted into ethylene oxide.

Catalyst selectivity, expressed as the number of moles of EO produced per mole of ethylene consumed, is a measure of the reactor performance and it shows how efficiently ethylene is used by the catalyst.

Catalyst selectivities have improved from 50 % to around 90 %. This has been achieved by optimising the support materials (e.g. aluminium oxide) and silver distribution, and by the use of promoters and moderators. Catalyst selectivity has a great impact on raw material consumption and the formation of carbon dioxide by-product.

Ageing of catalysts results in a decrease in activity and selectivity. Ageing may be caused by accumulation of catalyst poisons (e.g. sulphur from ethylene or methane), mechanical effects (e.g. abrasion, blocking of pores) and agglomeration of the silver particles; the latter may reduce the silver surface (and related catalyst activity) by 50 % which to a certain extent is compensated by raising the reaction temperature (e.g. to a maximum of 300 °C).

For fresh catalyst, improved selectivity brings not only higher EO yields, but also less heat generation which in turn increases catalyst lifetime. However, the catalysts with the highest selectivities tend to age more quickly and have to be replaced more frequently.
[90, Rebsdat et al. 2012], [41, CEFIC 2010].

7.4.3.1.2   Control of catalyst performance

Description
Control of catalyst performance in order to reduce the replacement frequency.

Technical description
Catalyst selectivity gradually decreases over time, resulting in increased raw material consumption per tonne of EO produced. Conceptually, lower raw material consumption over the lifetime of the catalyst could be achieved by more frequent catalyst changeout. In order to recognise a decrease in catalyst activity, updated balances of the reaction section are kept, based on suitable parameters such as the heat of reaction or the CO_2 formation.

Achieved environmental benefits
- Lower consumption of ethylene and oxygen.
- Lower emissions of CO_2 to air.

Cross-media effects
An increase in catalyst exchange frequency results in increased amounts of spent catalyst for recovery.

Economics
Benefits of maintaining a high catalyst performance include lower costs due to the reduced consumption of ethylene.

In terms of costs, increasing the catalyst exchange frequency implies higher catalyst costs and reduced economic performance from the reduced throughput due to the process downtime needed for the exchange of the catalyst.

The decision as to what level of performance will trigger the exchange of the catalyst will depend on an assessment also taking into account economic factors.

7.4.3.1.3   Use of inhibitors

The addition of an organochlorine inhibitor (such as ethylchloride or dichloroethane) to the reactor feed, in order to increase selectivity and reduce the proportion of ethylene that is fully oxidised to carbon dioxide, is common practice. According to the data collection, most plants use ethylchloride (0.5–2.5 kg/h).

The inhibitor will also be present in the recirculating process gas and may contribute to emissions to air via the inerts purge from the reaction cycle.

7.4.3.1.4   Process optimisation

The techniques that can be employed to reduce the specific ethylene consumption by limiting formation of carbon dioxide, losses of ethylene from the process or losses of ethylene oxide product are as follows:

Methane quality
The presence of heavy components can adversely affect the performance of the catalyst inhibitor, which can therefore increase the extent of carbon dioxide formation.

Construction materials
Aldehyde formation from ethylene oxide can be catalysed by a range of materials. The careful selection of construction materials (and possibly an appropriate maintenance regime) can therefore limit the formation of such impurities. However, the increase of ethylene consumption due to the formation of aldehydes is considered to be of only minor significance.

Reaction conditions
The selectivity of the process for ethylene oxide will be influenced by pressure, temperature, etc. The reaction conditions are optimised in a way that minimises carbon dioxide formation.

Raw material quality
Reducing the inert components in the ethylene and oxygen raw materials will limit the extent to which process gas needs to be purged in order to control the build-up of such inerts, and this will therefore limit the amount of ethylene that has to be wasted from the process. It may also limit the emissions of VOCs to air from the process where the purge stream is not used beneficially. However, the raw materials will need to be bought to general specifications, and there will therefore be a limitation on what can be achieved in this respect.

Dynamic control of purge rate
Having a sound basis for determining the required purge rate and ensuring that this is not exceeded is a key means of limiting the purge rate. Having a fixed purge rate may result in greater purge rates than may be really required.

The techniques that can be employed to reduce the specific ethylene consumption rate include the below techniques:

Glycol formation
Reducing the amount of ethylene glycols and heavy organics that are formed during ethylene oxide isolation will reduce ethylene consumption when judged in terms of ethylene oxide production. However, it is possible that some of the ethylene glycols formed could be used to supplement ethylene glycol production where ethylene oxide and/or ethylene glycols are produced at the same site.

Storage losses
The emissions of ethylene oxide from storage may be low not simply because of good venting design, but possibly because of good vent scrubbing arrangements. Recycling the spent scrubber liquor to the process to recover ethylene glycols reduces losses of product and reduces the load discharged to waste water treatment, although the effect may be low.

7.4.3.2   Techniques to reduce consumption of EO in EG production

The ethylene oxide consumption rate can be reduced by reducing the proportion of ethylene oxide that is transformed into heavy organics that leave as the bottom product from the final separation column, and which would ordinarily (but not necessarily) be considered a residue. The techniques that can be employed to reduce specific ethylene oxide consumption due to reducing heavy/heavier glycol formation under normal operating conditions include the following:

a)   Hydrolysis reaction optimisation
Using a significant water excess favours the formation of monoethylene glycol rather than the heavier glycols (see Section 7.4.5.2.1).

b)   Efficient fractionation

The more efficient the final separation columns, the lower the losses of glycols in their bottom product. In attempting to maximise the separation potential, it is possible that a higher energy demand will arise due to the use of an increased reflux ratio and/or higher vacuum.

7.4.4   Techniques to reduce energy consumption

Electricity and steam are the main utilities used in EO/EG plants and they usually represent a considerable share of production costs.

Setting a criteria or target

The reaction by-products generate energy. This leads to an interrelationship or trade-off between EO catalyst selectivity and heat balance: the more efficient the catalyst, the less steam that is produced in the EO reactors. Each installation (case by case) will decide whether energy or feedstock yield is more relevant.

The plant energy balance also depends on the relative sizes of the EO and EG sections. If the EO/EG process is a net steam exporter, the way to reuse this energy in the complex becomes of prime importance. To a certain extent, the EO/EG complex may play the role of a boiler plant for the site and this may hinder the use of more selective catalysts which would allow less steam to be exported.

The steam consumption of the EO/EG process is mainly due to distillation, and sometimes to turbines driving the gas compressors.

The methods for minimising the steam consumption of distillation when designing a new unit are well known. For existing distillation columns, retraying and repackaging techniques can be used, and technologies that often have a minor impact on steam consumption are principally used to debottleneck the capacity.

Unless steam turbines are used, the major electricity consumer of the EO/EG process is the recycle gas compressor at the EO unit. The usual ways to reduce the energy consumption of compressors are applicable (i.e. efficient design, reduction of pressure drops, etc.).

7.4.4.1   Fractionation

The techniques available for reducing the overall energy consumption associated with ethylene glycols dewatering and fractionation include the following:

Reduced water levels

Limiting the water excess in the glycols reaction will reduce the amount that needs to be evaporated off. However, this will likely increase the relative quantity of heavy glycols formed, and it will also have the knock-on effect of increasing the energy required by the subsequent fractionation step due to the need to progress more material through the chain of fractionation columns.

Hydrolysis of ethylene carbonate

Instead of hydrolysing ethylene oxide, hydrolysing ethylene carbonate requires a lower water excess and therefore would result in a lower overall energy consumption. The ethylene carbonate could be produced using the CO_2 isolated from the oxygen process (CO_2 is liberated during the hydrolysis, so it can be recycled), although this would require particular process conditions.

Evaporation configuration
The use of a multiple-effect evaporator would be more energy-efficient by allowing the steam use to be reduced. This may involve the need for vacuum pumps and/or vapour recompression.

Distillation column design
A column with a good inherent separation capability (due to efficient packing, height, etc.) may reduce the required reflux ratio, thereby reducing the vaporisation energy requirement during the fractionation.

Heat integration between distillations systems
This technique involves using heat from one column as a (partial) input of heat to another column – potential differences in vacuum levels might affect temperature differences. This may be done with the support of methodologies such as the pinch analysis (between the EO and EG production units, and externally between the EO/EG complex and the surrounding facility).

Earlier designs utilised trays in this application. Current designs utilise structured packing and trays to increase capacity (only in the case of revamped units).

7.4.4.2 Energy from vacuum generation

Combination of steam ejectors and liquid ring pumps
The use of steam ejectors and liquid ring pumps in combination can be more energy-efficient.

Plant integrity
Reducing the number of leaks (which in this context are not considered as contributing to an other than normal operating condition) will reduce the quantity of non-condensables that need to be handled and therefore reduce the load of the vacuum systems.

7.4.5 Techniques to reduce waste generation

7.4.5.1 Techniques to consider on spent catalyst

Conceptually, the consumption of EO catalyst (in terms of t/t of EO produced) could be minimised by running the catalyst for a longer time before replacement with a fresh batch. However, an ageing catalyst gradually loses its selectivity and therefore has to be replaced. The frequency of replacement depends on the catalyst selection (see Section 7.4.3.1.1) and the control of its performance (see Section 7.4.3.1.2).

Typically, the spent EO catalyst is sent to an external reclaimer for recovery of the valuable silver. After silver reclamation, the inert carrier requires disposal.

7.4.5.2 Techniques to reduce organic wastes from EO and EG units

7.4.5.2.1 Hydrolysis reaction optimisation

Description
The relative amount of heavy glycols formed in the glycol unit can be influenced to some extent by varying the water to EO ratio in the glycol reactor feed.

Technical description
Higher water to EO ratios result in lower co-production of heavier glycols but on the other hand require more energy for the glycol dewatering. The enforcement of the hydrolysis reaction may not always be desirable due to the fact that it will also reduce the formation of the co-products DEG and TEG, which are usually sold.

Achieved environmental benefits
Reduced quantity of heavy glycols, possibly requiring disposal.

Environmental performance and operational data
For data on the amount of residue generated per tonne of ethylene oxide, see Sections 7.3.6.2 and 7.3.6.4.

Cross-media effects
Increased energy consumption for the glycol dewatering.

Technical considerations relevant to applicability
Generally applicable.

Economics
Higher water to EO ratios result in lower co-production of heavier glycols but on the other hand require more energy for the glycol dewatering.

Driving force for implementation
Economic benefits.

Example plants
In the questionnaires, almost all operators confirmed the use of control/optimisation of the hydrolysis ratio as a technique to prevent wastes.

Reference literature
No reference literature provided.

7.4.5.2.2   Isolation and sale of by-products from EO units

Description
The concentrated organic fraction obtained after the dewatering of the liquid effluent from EO recovery is distilled to give valuable short-chain glycols and a heavier residue (containing heavy glycols and organic salts) for sale or disposal (incineration).

Environmental performance and operational data
For data on the amount of residue generated per tonne of ethylene oxide, see Section 7.3.6.2.

Only one operator reported amounts of waste for disposal (incineration), which were in the range of only a few g/t of EO, which indicates for this site, too, that most of the residue is marketed.

Technical considerations relevant to applicability
Depending on the design, the implementation of the technique at an existing EO plant may imply a major revamp and investment, with a potentially lower performance in terms of energy efficiency and product quality.

In terms of waste reduction, there is no need for the isolation of by-products if the organic fraction can be marketed as a whole.

Example plants
According to the questionnaires, at most of the sites the residue from the EO purification is sold. Some operators answered that they would incinerate residues from the EO and/or EG unit if they could not be sold.

7.4.5.2.3   Isolation of by-products from EG units for sale

Description
For EG units, the heavy glycols fraction can either be sold as such or further fractionated to yield pure valuable glycols.

Technical description
The bottom stream of the last distillation column of the glycol fractionation unit contains the higher boiling ethylene glycols (heavy glycols). The composition of this stream depends on the extent of separation of the lower boiling glycol products. Typical compounds are triethylene glycol, tetraethylene glycol and higher ethylene glycols.

The stream can be either sold as such or fractionated to yield pure marketable glycols. If the stream is not marketed as such, the recovery of glycols is maximised, in order to minimise the waste to be disposed of.

Environmental performance and operational data
For data on the amount of residue generated per tonne of ethylene oxide, see Section 7.3.6.4.

Only one operator reported amounts of waste for disposal (incineration), which were in the range of only a few g/t of EO, which indicates for this site, too, that most of the residue is marketed.

Technical considerations relevant to applicability
In terms of waste reduction, there is no need for the isolation of by-products if the organic fraction can be marketed as a whole.

Example plants
According to the questionnaires, at most sites (i.e. all sites that provided information), the heavy glycol residues from the EG unit are marketed. Some operators answered that they would incinerate residues from the EO and/or EG unit if they could not be sold.

7.5 Emerging techniques

7.5.1 Co-production of diphenyl carbonate (DPC) and ethylene glycol

Description
Carbon dioxide, phenol and ethylene oxide react to form DPC and ethylene glycol.

The main product is DPC (mainly for the production of polycarbonate), and the environmental benefits relate to the production of DPC by a phosgene-free route. In the context of the EO/EG process, the co-production of EG may substitute some part of the EG directly produced from EO.

Alternatively, the process can be carried out with propylene oxide instead of ethylene oxide which then would not be related to EG production.

Commercially developed
By Shell.

Level of environmental protection
Environmental benefits are:

- substitution of phosgene (avoiding the emissions and safety issues related to phosgene production and handling);
- consumption/transformation of carbon dioxide.

When it might become commercially available
In a few years; pilot plant in operation.

References
[105, Shell 2011].

7.5.2 MEG production via dimethyl oxalate

Description
Monoethylene glycol (MEG) is produced by the reduction of dimethyl oxalate (DMO) with hydrogen. DMO is obtained by a more complex process from carbon monoxide (syngas) which allows the production to be based on coal (alternatively natural gas or possibly biomass) as the carbon source instead of ethylene.
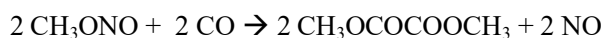
The process implies the following steps:

1) Synthesis/regeneration of methyl nitrite from methanol and nitrogen oxide:

$$2\ NO + 0.5\ O_2 + 2\ CH_3OH \rightarrow 2\ CH_3ONO + H_2O$$

Gas-liquid reaction. Small losses of NO may occur by oxidation.

2) Synthesis of DMO by carbonylation of methyl nitrite:

$$2\ CH_3ONO + 2\ CO \rightarrow 2\ CH_3OCOCOOCH_3 + 2\ NO$$

Catalysed gas-phase reaction (e.g. using Pd), condensation of DMO (e.g. by scrubbing with methanol).

3) Production of MEG:

$$CH_3OCOCOOCH_3 \;\; + 4\,H_2 \rightarrow CH_2OHCH_2OH + 2\,CH_3OH$$

Catalysed vapour-phase process, e.g. using Cu-Cr-BA- or Cu-Cr-Zn-based catalyst, followed by multistep distillation to remove organic impurities (e.g. methyl glycolate, dimethyl carbonate, methyl formate, 1,2-butanediol).

Methanol and NO are recycled within the process. The resulting total balance is:

$$2\,CO + 0.5\,O_2 + 4\,H_2 \rightarrow CH_2OHCH_2OH + H_2O$$

Level of environmental protection
No information provided. A comprehensive environmental process evaluation would have to consider all process steps starting with the upstream non-LVOC processes.

The LVOC process is more complex and involves other potential pollutants. Therefore there is no straightforward indication that emissions will be lower compared to the production of glycol from ethylene oxide.

When it might become commercially available
Soon, driven by the interest in having coal-based processes in China. A pilot plant is in operation. In 2011 Henan Coal Chemical group and Tomgliao Jinmei Chemical Industry announced plans to produce 1.8 million tonnes in China, starting with four installations with capacities of 200 kt/yr each in 2011.

References
[104, Naqvi 2013], [104, Naqvi 2013], [103, Nexant Inc 2011].