

## **7.23 Manufacture of organic chemicals (Except production of organic fine chemicals, chapter 7.24)**

### **7.23.1 Coverage**

In this chapter, the organic chemical industry is the industry aiming at producing the following types of products :

- Lower olefins such as ethylene and propylene produced mainly by the steam cracking route,
- Aromatics compounds such as benzene and toluene,
- Oxygenated compounds,
- Nitrogenated compounds,
- Halogenated compounds,
- Polymers (polyethylene, polypropylene, PVC, polyesters, polystyrene...).

### **7.23.2 Emission sources**

In the production of organic chemicals, emissions differ widely according to the products and production processes. Often one product is produced by different processes, each of which has its own emission characteristics with regard to VOCs.

VOCs emissions arise from some main sources, as follows:

- Fugitive emissions. Fugitive VOC emissions are released from leaking pressurised equipment components on process units, such as valves, flanges and connectors, opened lines and sampling systems containing volatile liquids or gases. Volatile products are defined in CEN 15446 [7] and reference [8] as all products of which at least 20% by weight has a vapour pressure higher than 0,3 kPa at 20°C,
- Stack emissions,
- Flaring systems (used for safe disposal of hydrocarbons or hydrogen that cannot be recovered in the process),
- Storage and handling of chemical substances treated in chapter 7.22.

### **7.23.3 BAT, Associated Emission Levels (AEL)**

#### **New installations:**

When new processes are designed and in case of major modification of existing processes, BAT is a selection of the following techniques:

- Carry out chemical reactions and separation processes continuously, in closed equipment,
- Subject continuous purge streams from process vessels to the hierarchy of: re-use, recovery, combustion in air pollution control equipment and combustion in non dedicated equipment
- Minimise energy use and maximise energy recovery,
- Use compounds with low or lower vapour pressure.

Process modification, including changes of feedstock and products, can in selected cases help to reduce NMVOC emissions. New chemical reactions or principles may be applied to reduce the quantity of undesired by-products. Process improvements must also aim at recovery and recycling of by-products as well as at enclosing open process equipment as far as possible.

An efficient measure to reduce waste gas flow rates and NMVOC emissions from oxidation and oxychlorination processes (e.g. production of vinyl chloride) is the use of pure oxygen instead of air. New oxidation and oxychlorination plant usually uses only pure oxygen.

### **Fugitive VOC emissions:**

For preventing and controlling fugitive VOC emissions, BATs are a combination of leak detection and repair programme as the use high performance equipment:

- A leak detection and repair programme consisting in measuring the concentration of VOC in the atmosphere around the potential leak, then selecting equipments leaking over a defined threshold value and finally operating a repair on those leaking items.

A LDAR programme is established according to the following principles [6]:

- The definition of what constitutes a leak and fixation of corresponding thresholds,
- The fixation of the frequency of inspections,
- The listing and identification of components included,
- The procedures concerning repair of leaking components depending of the leak category.

Immediate minors repair can be carried out immediately such as tightening leaking equipment. Maintenance and complex repair have to be scheduled. They can be done during scheduled shutdown.

Equipment tightening can be made with equipment in operation (except with remote control valves (eg tightening bolts to eliminate leaks from valves stems or flanges, installing tightening caps on open ends...)).

Maintenance with dismantling equipment or exchange, can only be carried out during plant shutdowns with circuits insulation and degassing. So, during plant shutdowns, two kinds of maintenance programme can be carried out according to the situation [6]:

- Basic maintenance: maintenance on the equipment (flanges + valves) to remove some parts or to change the equipment with a new one of the same technology.
  - Heavy maintenance: complete change of the valves with valves of the higher grade standard, not leaking technology. Basic maintenance is maintained for the flanges.
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- Use high performance equipment such as [1]:
  - Valves: low leak rate valves with double packing seals, bellow seals for high risk duty,
  - Pumps: double seals with liquid or gas barrier, or seal pumps,
  - Compressors and vacuum pumps: double seals with liquid or gas barrier, or seal less pumps, or simple seal technology with equivalent emission levels,
  - Flanges: minimise the number, use effective gaskets,
  - Open ends: fir blind flanges, caps and plugs to infrequently used fittings, use closed loop flush on liquid sampling points, and for sampling systems analysers optimise the sampling volume/frequency, minimise the length of sampling lines or fit enclosures,
  - Safety valves: fit upstream rupture disk.

### **Stack VOC emissions:**

VOC in vent gases can be controlled by conventional methods of controlling organic pollutants from stationary sources, i.e. adsorption, absorption, condensation, membrane process, thermal and catalytic incineration, as well as process modification. These techniques are presented in chapter 5.3.2.

### **Flare emissions:**

- For preventing flare emissions, BAT is:
- Minimise the need for hydrocarbon disposal to flare through good plant design and good plant management
- BAT for elevated flare design and operation includes the provision of permanent pilots and pilots flame detection, efficient mixing, ratio controlled to the hydrocarbon flow and remote monitoring by closed circuit television
- Destruction efficiency larger than 99% for elevated flare and 99.5 % for ground flares.

### **VOC from storage, handling and transfer [1] and [2]:**

BAT for **storage, handling and transfer** is, in addition to those described in chapter 7.22, an appropriate combination or selection of, *inter alia*, the following techniques:

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

### **7.23.4 Cost data for emission reduction techniques**

Unit costs range from -100 to + 180 €/t VOC abated according to the reduction measure considered according to EGTEI [9] for implementing a LDAR programme to reduce fugitive emissions for the steam cracking unit. Negative costs indicate that savings are high and counter balance.

Unit costs range can be much larger and range as example from 310 to 1050 €/t VOC abated according to the reduction measure considered in the production of PVC [10].

### **7.23.5 References used for chapter 7.23**

[1] European Commission - Reference document on BAT in the large volume organic chemical industry – February 2003

[2] European Commission - Reference document on BAT in the production of polymers – 2006

[3] European Commission - Reference document on BAT for the manufacture of organic fine chemicals August 2006

[4] European Commission - reference document on BAT in common waste water and waste gas treatment / management systems in the chemical sector – February 2003.

[5] European Commission - reference document on BAT in storage to be completed – February 2003.

[6] EGTEI background document on the organic chemical industry.

[7] EN15446:2008 Fugitive and diffuse emissions of common concern to industry sectors - Measurement of fugitive emission of vapours generating from equipment and piping leaks

[8] EPA - Protocol for equipment leak - Emission estimates EPA 453-95-017 – 1995

[9] EGTEI - Organic chemical industry – steam cracking – synopsis sheet - 15 October 2005

<http://www.citepa.org/forums/egtei/10-Synopsis-sheet-steam-cracking-15-10-05.pdf>

[10] EGTEI - Organic chemical industry – Production of PVC – synopsis sheet - 3 October 2005

<http://www.citepa.org/forums/egtei/11-synopsis-sheet-PVC-suspension-03-10-05.pdf>

