7.24 Production of organic fine chemicals

7.24.1 Coverage

The speciality organic chemical industry covers the production of different types of chemicals produced in campaign basis, in multi purpose and multi product plants (pharmaceutical active ingredients, biological products, food additives, photographic chemicals, dyestuffs and intermediates, pesticides and other speciality products…) [1].

The pharmaceutical product manufacturing is part of the organic chemical industry and covers both:

- The production of primary pharmaceutical products: production of bulk pharmaceuticals, drug intermediates and active ingredients by means of synthesis, fermentation, extraction or other processes, in multipurpose and multi product plants and on a campaign basis.
- The activities related to formulation of finished drugs and medicines using the active ingredients supplied by the bulk plants (taking place in finishing plants). Active ingredients are converted into products suitable for administration. Physical formulation, filling and packaging are involved.

Only VOC emissions are covered in this chapter.

7.24.2 Emission sources

This industry is very heterogeneous: plants manufacture a large range of products, using a large number of production processes and may store and use several hundred raw material substances or intermediate products. Processes are usually operated on a campaign basis and in multi purpose plants. For one active ingredient, several transformation stages are required. The processes typically involve between 1 to 40 transformation stages depending on molecules. Process stages cover the full range of unit operations such as: reactions, liquid/liquid extraction, liquid/liquid or liquid/solid or gas/solid separation, distillation, crystallisation, drying, gas adsorption… Production is carried out in discontinuous processes (or batch processes). Equipment is rarely specific but, most often, multi application. Processes frequently use solvents. Any reacted raw materials may be either recovered or recycled or ultimately discharged to the environment after appropriate treatment.

Due to the diversity of processes used in this sector, no simple process description can be made. Instead, a brief outline of characteristics of existing pharmaceutical product production plants is provided.

Significant number of VOC emission release points

Gaseous discharge circuits are complex. For the same equipment, several discharge points often exist, depending on the performed operations. The large number of discharge points is due to:

- Quality constraints required in this sector in order to avoid risks of cross-contamination,
- Security constraints in order, for example, to avoid the contact of incompatible gases.

Plants having an annual solvent consumption ranging from 900 to 1 500 t may have from 10 to 50 VOC emission vent stacks in the atmosphere.

A large number of discharge points are equipped with condensers to trap VOCs. To trap corrosive or toxic gases, several vents are related to abatement absorption columns. When secondary abatement techniques are applied, collecting the vents proves to be necessary.

High variability of VOC discharges with time

VOC concentrations may vary widely from one discharge point to another. Discharges with high waste gas flow rates and low concentrations do exist; general ventilation of a factory belongs to this group. Other discharges, such as production equipment vents are characterised by very low waste gas flow rates (some Nm^3/h) and VOC concentrations that may be high.

VOC discharges present a very high variability over time: high variability over time when there is a discharge and non-permanent discharges.

This situation leads to more significant costs for emission treatment: the gas-cleaning device should be able to accept emission peaks. Abatement technique dimensioning must be based on the peak discharge (the frequency of peaks should be considered as well). Investments are thus higher than for more regular emissions in time.

A large number of solvents used

In this activity, even though 5 solvents (methanol, toluene, acetone, ethanol, methane dichloride) represent about 70 % of the new solvent consumption [1], around 40 different solvents are in use. The consumption of chlorinated solvents is still quite high. This large number of solvents, the presence of chlorinated solvents and security and quality constraints make the use of secondary abatement techniques more difficult and more expensive (treatment of HCl if incineration, limited potential for collection and recycling of solvents).

7.24.3 BAT, Associated Emission Levels (AEL)

In order to reduce solvent losses and emissions into the atmosphere, a wide range of best practices and process improvements are available among which work in concentrated environment in order to reduce the consumption of solvents, increased use of low volatile solvents and of solvents easier to condense, modification of certain operating conditions for distillation (e. g. distillation under ordinary pressure instead of vacuum distillation), implementation of good housekeeping, increased condenser efficiency (increased exchanger surfaces and increased refrigerating capacities), technology change (dry-sealed vacuum pumps instead of liquid ring vacuum pumps; closed pressure filters or vacuum filters more leak free than open filters; vacuum dryers leading to a better solvent condensation…).

A list of BAT is a follows [2]:

- Contain and enclose sources and close any openings in order to minimise uncontrolled emissions,
- Carry out drying using closed circuits, including condensers for solvent recovery,
- Keep equipment closed for rinsing and cleaning with solvents,
- Close unnecessary openings in order to prevent air being sucked to the gas collection system via the process equipment,
- Ensure the air tightness of process equipment, especially of vessels,
- Apply shock inertisation instead of continuous inertisation,
- Minimise the exhaust gas volume from distillations by optimisation of the layout of the condenser,
- Carry out liquid addition into vessels as bottom feed or with dip leg, unless reaction chemistry and / or safety considerations make it impractical. In such cases, the addition of liquid as top feed with a pipe directed to the wall reduces splashing and hence the organic load of the displaced gas,
- Minimise the accumulation of peak loads and flows and related concentration peaks by optimisation of the production matrix and application of smoothing filters.
- Treatment of waste gases containing VOC. The selection of VOC treatment techniques is a crucial task on a multipurpose site. Since the volume flows show a wide variation on a mltipurpose site, the key parameter for the selection of techniques are average mass flows from emission point sources in kg/hour. One or a combination of techniques can be applied as a recovery/abatement system for a whole site, an individual production building, or an individual process. This depends on the particular situation and affects the number of point sources. Non-oxidative recovery/abatement techniques are operated efficiently after minimisation of volume flows and the achieved concentration levels should be related to the corresponding volume flow without dilution by, e.g. volume flows from building or room ventilation. Thermal oxidation/incineration and catalytic oxidation are proven techniques for destroying VOCs with highest efficiency but show considerable cross-media effects. In direct comparison, Catalytic oxidation consumes less energy and creates less NOX and hence is preferred where technically possible. Thermal oxidation is advantageous where support fuel can be replaced by organic liquid waste (e.g. waste solvents which are technically/economically available on-site and non-recoverable) or where autothermal operation can be enabled by stripping of organic compounds from waste water streams. Where exhaust gases also contain high loads of other

pollutants besides VOCs, thermal oxidation can enable, e.g. the recovery of marketable HCl or, if the thermal oxidiser is equipped with a DeNOX unit or is designed as two stage combustion, the efficient abatement of NOX .Thermal oxidation/incineration and catalytic oxidation can also be a suitable technique to reduce odour emissions.

BAT is to reduce emissions to the levels given
Existing installations can reduce their total VOC emissions to less than 5 % of the solvent input by following a combined strategy which involves:
a) Step-by-step implementation of integrated measures to prevent/reduce diffuse/fugitive emissions and to minimise the mass flow that requires abatement
b) Applying high level recovery/abatement techniques, such as thermal/catalytic oxidation or activated carbon adsorption
c) Applying specific recovery/abatement techniques at source on smaller sites with dedicated equipment, and by utilising only one or two different bulk solvents.

Table 1: selected VOC control measures with BAT associated VOC emission levels for organic fine chemicals

Emission source	Combination of control measures	BAT associated emission levels for VOC
New plants	Mix of BAT defined above (primary measures and use of secondary measures (both oxidation, adsorption and / or condensation))	≤ 3 % of solvent input*
Existing plants	Mix of BAT defined above (primary measures and use of secondary measures (both oxidation, adsorption and / or condensation))	≤ 5% of solvent input*

* Sum of I1 the quantity of organic solvents or their quantity in preparations purchased which are used as input into the process in the time frame over which the mass balance is being calculated + I2 the quantity of organic solvents or their quantity in preparations recovered and reused as solvent input into the process. (The recycled solvent is counted every time it is used to carry out the activity.)

Table 2: BAT Associated VOC Emission Levels for non-oxidative recovery/abatement techniques [2]

Process step	Average emission level from point sources*
Non-oxidative recovery/abatement techniques	0.1 kg C/hour* or 20 mg C/m3**
*The averaging time relates to the emission profile, the levels relate to dry gas and Nm3 **The concentration level relates to volume flows without dilution by, e.g. volume flows from room or building ventilation	

Table 3: BAT associated emission levels for total organic C for thermal oxidation/incineration or catalytic oxidation [2]

Process step	Average emission level from point sources*		
Thermal oxidation/incineration or catalytic oxidation	Average mass flow < 0.05 kg C/h**	or	Average concentration**

			< 5 mg C/m^3
* The averaging time relates to the emission profile, levels relate to dry gas and Nm^3 ** These values are technically demanding and attention has to be carried out on energy efficiency which might be not acceptable			

7.24.4 Cost data for emission reduction technique

Costs vary in a large range. Average investments to achieve best performance levels on an existing plant are about 6700 k€ and the total costs per kg of abated VOC of 2.3 €/kg [8].

7.24.5 Reference used for chapter 7.24

[1] Speciality organic chemical industry. EGTEI background document – 24 may 2005

http://www.citepa.org/forums/egtei/speciality_chemistry_290405.pdf

[2] European commission - reference document on BAT for the manufacture of organic fine chemicals August 2006

[3] Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31999L0013:EN:HTML

[4] Regulation (EC) No 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC

[5] Arrêté du 31 janvier 2008 relatif au registre et à la déclaration annuelle des émissions polluantes et des déchets - (JO n° 62 du 13 mars 2008)

[6] Comments from André Peeters Weem, Cees Braams from InfoMil, the Dutch Ministry of Environment on GD 7-26 Manufacture of organic fine chemical - version 1

[7] Comments from Johannes Drotleff, German Umweltbundesamt on GD 7-26 Manufacture of organic fine chemical - version 1

[8] Speciality organic chemical industry. Synopsis sheet – 3 October 2005

http://www.citepa.org/forums/egtei/31-Synopsis-sheet-Speciality-organic-chemical-industry-03-10-05.pdf