Integrated Pollution Prevention and Control

Reference Document on
Best Available Techniques in the Production of

Polymers

Dated October 2006
EXECUTIVE SUMMARY

1) Introduction
The BAT (Best Available Techniques) Reference Document (BREF) entitled “Best Available Techniques for the Production of Polymers” (POL) reflects an information exchange carried out under Article 16(2) of Council Directive 96/61/EC (IPPC Directive). This executive summary describes the main findings, a summary of the principal BAT conclusions and the associated emission and consumption levels. It should be read in conjunction with the preface, which explains this document’s objectives; how it is intended to be used and legal terms. It can be read and understood as a standalone document but, as a summary, it does not present all the complexities of this full document. It is therefore not intended as a substitute for this full document as a tool in BAT decision making.

2) Scope of this document
This document focuses on the main products of the European polymer industry both in production figures and in environmental impact, mainly produced in dedicated installations for the production of one specific polymer. The list of products covered is not conclusive but includes polyolefins, polystyrene, polyvinyl chloride, unsaturated polyesters, emulsion polymerised styrene butadiene rubbers, solution polymerised rubbers containing butadiene, polyamides, polyethylene terephthalate fibres and viscose fibres.

For polymer production installations, no specific threshold was established in drawing a borderline between IPPC installations and non IPPC installations as this is not foreseen in the IPPC Directive.

3) The sector and environmental issues
Polymer companies produce a variety of basic products, which range from commodities to high added-value materials and are produced in both batch and continuous processes covering installations with a capacity of some 10000 tonnes per year up to some 300000 tonnes per year.

The basic polymers are sold to processing companies, serving an immense range of end-user markets.

The chemistry of polymer production consists of three basic reaction types, polymerisation, polycondensation and polyaddition, thus the number of operations/processes used remains reasonably small. These include preparation, the reaction itself and the separation of products. In many cases cooling, heating, or the application of vacuum or pressure is necessary. The unavoidable waste streams are treated in recovery and/or abatement systems or disposed of as waste.

The key environmental issues of the polymer sector are emissions of volatile organic compounds, in some cases waste waters with the potential for high loads of organic compounds, relatively large quantities of spent solvents and non-recyclable waste as well as the energy demand. Given the diversity of the sector and the wide range of polymers produced, this document does not provide a complete overview of the releases from the polymer sector. However, emission and consumption data are presented from a broad range of currently operational plants in the sector.

4) Techniques to consider in the determination of BAT
The techniques to consider in the determination of BAT are grouped in a generic section and product specific sections for certain polymers. The former includes environmental management tools, equipment design and maintenance, monitoring and some generic techniques related to energy and end-of-pipe measures.
5) Best available techniques
The summary presented below does not include background statements and cross referencing which is found in the full text. Additionally, the full text contains BAT on environmental management which is not mentioned in this executive summary.

**The interface with the BREF on CWW**
The BREF on “Common waste gas and waste water treatment/management systems in the chemical sector” describes techniques which are commonly applicable to the whole spectrum of the chemical industry. Detailed descriptions of recovery or abatement techniques can be found in the BREF on CWW.

The BAT associated emission levels of the end-of-pipe techniques described in the CWW BREF are BAT wherever these techniques are applied in the polymer sector.

**Mass flow and concentration levels**
This document mostly refers to production related BAT associated emission and consumption levels, and also refers to end-of-pipe techniques whose concentration related performance can be found in the CWW BREF. All BAT associated emission levels relate to total emissions including both point sources and fugitive emissions.

**Understanding the application of the BAT**
The BAT that are listed include generic BAT and specific BAT for the different polymers covered in this document. The generic BAT are those that are considered to be generally applicable to all types of polymer installations. The polymer specific BAT are those that are considered to be specifically BAT for installations dealing mainly or wholly with certain types of polymers.

**Generic BAT is**

- to reduce fugitive emissions by advanced equipment design including:
  - use of valves with bellow or double packing seals or equally efficient equipment. Bellow valves are especially recommended for highly toxic services
  - magnetically driven or canned pumps, or pumps with double seals and a liquid barrier
  - magnetically driven or canned compressors, or compressors using double seals and a liquid barrier
  - magnetically driven or canned agitators, or agitators with double seals and a liquid barrier
  - minimisation of the number of flanges (connectors)
  - effective gaskets
  - closed sampling systems
  - drainage of contaminated effluents in closed systems
  - collection of vents.

- to carry out a fugitive loss assessment and measurement to classify components in terms of type, service and process conditions to identify those elements with the highest potential for fugitive loss

- to establish and maintain an equipment monitoring and maintenance (M&M) and/or leak detection and repair (LDAR) programme based on a component and service database in combination with the fugitive loss assessment and measurement
• to reduce dust emissions with a combination of the following techniques:
  o dense phase conveying is more efficient to prevent dust emissions than dilute phase conveying
  o reduction of velocities in dilute phase conveying systems to values as low as possible
  o reduction of dust generation in conveying lines through surface treatment and proper alignment of pipes
  o use of cyclones and/or filters in the air exhausts of dedusting units. The use of fabric filter systems is more effective, especially for fine dust
  o use of wet scrubbers.

• to minimise plant start-ups and stops to avoid peak emissions and reduce overall consumption (e.g. energy, monomers per tonne of product)
• to secure the reactor contents in case of emergency stops (e.g. by using containment systems)
• to recycle the contained material or to use it as fuel
• to prevent water pollution by appropriate piping design and materials. To facilitate inspection and repair, effluent water collection systems at new plants and retrofitted systems are, e.g.:
  o pipes and pumps placed above ground
  o pipes placed in ducts accessible for inspection and repair.

• to use separate effluent collection systems for:
  o contaminated process effluent water
  o potentially contaminated water from leaks and other sources, including cooling water and surface run-off from process plant areas, etc.
  o uncontaminated water.

• to treat the air purge flows coming from degassing silos and reactor vents with one or more of the following techniques:
  o recycling
  o thermal oxidation
  o catalytic oxidation
  o adsorption
  o flaring (only discontinuous flows).

• to use flaring systems to treat discontinuous emissions from the reactor system. Flaring of discontinuous emissions from reactors is only BAT if these emissions cannot be recycled back into the process or used as fuel
• to use, where possible, power and steam from cogeneration plants. Cogeneration is normally installed when the plant uses the steam produced, or where an outlet for the steam produced is available. The electricity produced can either be used by the plant or exported
• to recover the reaction heat through the generation of low pressure steam in processes or plants where internal or external consumers of the low pressure steam are available
• to re-use the potential waste from a polymer plant
• to use pigging systems in multiproduct plants with liquid raw materials and products
• to use a buffer for waste water upstream of the waste water treatment plant to achieve a constant quality of the waste water. This applies to all processes producing waste water, such as PVC and ESBR
• to treat waste water efficiently. Waste water treatment can be carried out in a central plant or in a plant dedicated to a special activity. Depending on the waste water quality, additional dedicated pretreatment is required.
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BAT for polyethylene is

- to recover monomers from reciprocating compressors in LDPE processes to:
  - recycle them back to the process and/or
  - send them to a thermal oxidiser.
- to collect off-gases from the extruders. Off-gases from the extruding section (extruder rear seal) in LDPE production are rich in VOC. By sucking off the fumes from the extrusion section, the emission of monomers is reduced
- to reduce the emissions from finishing and storage sections by treatment of purge air
- to operate the reactor at the highest possible polymer concentration. By increasing the concentration of the polymer in the reactor, the overall energy efficiency of the production process is optimised
- to use closed-loop cooling systems.

BAT for LDPE is

- operation of the low pressure separator (LPS) vessel at minimum pressure and/or
- solvent selection and
- devolatilisation extrusion or
- treatment of purge air from degassing silos.

BAT for suspension processes is

- application of closed-loop nitrogen purge systems and
- optimisation of the stripping process and
- recycling of monomers from the stripping process and
- condensation of the solvent and
- solvent selection.

BAT for gas phase processes is

- application of closed-loop nitrogen purge systems and
- solvent and comonomer selection.

BAT for solution LLDPE processes is

- condensation of the solvent and/or
- solvent selection and
- devolatilisation extrusion or
- treatment of purge air from degassing silos.

BAT for polystyrene is

- to reduce and control emissions from storage by one or more of the following techniques:
  - minimisation of level variation
  - gas balance lines
  - floating roofs (large tanks only)
  - installed condensers
  - vent recovery to treatment.
• to recover all purge streams and reactor vents
• to collect and treat the exhaust air from pelleting. Usually, the air sucked off the pelleting section is treated together with reactor vents and purge streams. This only applies to GPPS and HIPS processes
• to reduce emissions from the preparation in EPS processes by one or more of the following or equivalent techniques:
  o vapour balance lines
  o condensers
  o vent recovery to further treatment.

• to reduce emissions from the dissolving system in HIPS processes by one or more of the following techniques:
  o cyclones to separate conveying air
  o high concentration pumping systems
  o continuous dissolving systems
  o vapour balance lines
  o vent recovery to further treatment
  o condensers.

**BAT for polyvinyl chloride is**

• to use appropriate storage facilities for the VCM feedstock, designed and maintained to prevent leaks and resulting air, soil and water pollution:
  o to store VCM in refrigerated tanks at atmospheric pressure or
  o to store VCM in pressurised tanks at ambient temperature and
  o to avoid VCM emissions by providing tanks with refrigerated reflux condensers and/or
  o to avoid VCM emissions by providing tanks with connection to the VCM recovery system or to appropriate vent treatment equipment.

• to prevent emissions from connections when unloading VCM by
  o use of vapour balance lines and/or
  o evacuation and treatment of VCM from connections prior to decoupling

• to reduce residual VCM emissions from reactors by an appropriate combination of the following techniques:
  o reducing the frequency of reactor openings
  o depressurising the reactor by venting to VCM recovery
  o draining the liquid contents to closed vessels
  o rinsing and cleaning the reactor with water
  o draining of this water to the stripping system
  o steaming and/or flushing the reactor with inert gas to remove residual traces of VCM, with transfer of the gases to VCM recovery.

• to use stripping for the suspension or latex to obtain a low VCM content in the product
• to treat waste water with a combination of:
  o stripping
  o flocculation
  o biological waste water treatment.
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• to prevent dust emissions from drying process with cyclones for suspension PVC, bag filters for microsuspension and multiple bag filters for emulsion PVC
• to treat VCM emissions from the recovery system by one or more of the following techniques:
  o absorption  
  o adsorption  
  o catalytic oxidation  
  o incineration.

• to prevent and control fugitive emissions of VCM arising from equipment connections and seals  
• to prevent accidental emissions of VCM from polymerisation reactors by one or more of the following techniques:  
  o specific control instrumentation for reactor feeds and operational conditions  
  o chemical inhibitor systems to stop the reaction  
  o emergency reactor cooling capacity  
  o emergency power for agitation (water insoluble catalysts only)  
  o controlled emergency vent capacity to the VCM recovery system.

BAT for unsaturated polyesters is

• to treat exhaust gases by one or more of the following techniques:  
  o thermal oxidation  
  o activated carbon  
  o glycol scrubbers  
  o sublimation boxes.

• to thermally treat waste water, arising mainly from the reaction (mostly together with waste gas).

BAT for ESBR is

• to design and maintain the plant storage tanks to prevent leaks and resulting air, soil and water pollution and to use one or more of the following techniques for storage:  
  o minimise level variation (integrated plants only)  
  o gas balance lines (nearby tanks only)  
  o floating roofs (large tanks only)  
  o vent condensers  
  o improved styrene stripping  
  o vent recovery to external treatment (usually incineration).

• to control and minimise diffuse (fugitive) emissions by the following or equivalent techniques: 
  o monitoring of flanges, pumps, seals, etc.  
  o preventive maintenance  
  o closed-loop sampling  
  o plant updates: tandem mechanical seals, leak proof valves, improved gaskets.
to collect the vents from process equipment for treatment (usually incineration)
• to recycle water
• to treat waste water using biological treatment or equivalent techniques
• to minimise the volume of hazardous waste by good segregation and collect them to send for external treatment
• to minimise the volume of non-hazardous waste by good management and off-site recycling.

**BAT for solution polymerised rubbers containing butadiene is**

• to remove solvents from the product by using one or both of the following or an equivalent technique:
  o devolatilisation extrusion
  o steam stripping.

**BAT for polyamides is**

• to treat flue-gases from polyamide production processes by wet scrubbing.

**BAT for polyethylene terephthalate fibres is**

• to apply a waste water pretreatment such as one or more of the following techniques:
  o stripping
  o recycling
  o or equivalent

  before sending waste water from PET production processes to a WWT plant

• to treat waste gas streams from PET production with catalytic oxidation or equivalent techniques.

**BAT for viscose fibres is**

• to operate spinning frames in houses
• to condense the exhaust air from spinning streets to recover CS$_2$ and recycle it back into the process
• to recover CS$_2$ from exhaust air streams through adsorption on activated carbon. Depending on the concentration of H$_2$S in the exhaust air, different technologies are available for the adsorptive recovery of CS$_2$
• to apply exhaust air desulphurisation processes based on catalytic oxidation with H$_2$SO$_4$ production. Depending on the mass flows and concentrations, there are a number of different processes available to oxidise exhaust gases containing sulphur
• to recover sulphate from spinning baths. BAT is to remove sulphate as Na$_2$SO$_4$ from the waste water. The by-product is economically valuable and sold
• to reduce Zn from the waste water by alkaline precipitation followed by sulphide precipitation
• to use anaerobic sulphate reduction techniques for sensitive waterbodies
• to use fluidised bed incinerators to burn non-hazardous wastes and recover the heat for the production of steam or energy.
6) BAT associated emission and consumption levels

Taking into account the generic and specific BAT, the following emission and consumption levels are associated with BAT (see the following table):

<table>
<thead>
<tr>
<th></th>
<th>VOC (g/t)</th>
<th>Dust (g/t)</th>
<th>COD (g/t)</th>
<th>Suspended solids (g/t)</th>
<th>Direct energy (GJ/t)</th>
<th>Hazardous waste (kg/t)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Existing: 1100 - 2100</td>
<td></td>
<td></td>
<td></td>
<td>Autoclave: 3.24 – 3.60</td>
<td>1.8 – 3.0</td>
</tr>
<tr>
<td></td>
<td>LDPE copolymers</td>
<td>2000</td>
<td>20</td>
<td></td>
<td></td>
<td>4.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>LDPE</td>
<td>New: 300 - 500</td>
<td>56</td>
<td>17</td>
<td></td>
<td>New: 2.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Existing: 500 - 1800</td>
<td></td>
<td></td>
<td></td>
<td>Existing: 2.05 – 2.52</td>
<td>3.1</td>
</tr>
<tr>
<td>LLDPE</td>
<td>New: 200 - 500</td>
<td>11</td>
<td>39</td>
<td></td>
<td>New: 2.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Existing: 500 - 700</td>
<td></td>
<td></td>
<td></td>
<td>Existing: 2.08 – 2.45</td>
<td>0.8</td>
</tr>
<tr>
<td>GPPS</td>
<td>85</td>
<td>20</td>
<td>30</td>
<td>10</td>
<td>1.08</td>
<td>0.5</td>
</tr>
<tr>
<td>HIPS</td>
<td>85</td>
<td>20</td>
<td>30</td>
<td>10</td>
<td>1.48</td>
<td>0.5</td>
</tr>
<tr>
<td>EPS</td>
<td>450 - 700</td>
<td>30</td>
<td></td>
<td></td>
<td>1.80</td>
<td>3.0</td>
</tr>
<tr>
<td>S-PVC</td>
<td>VCM: 18 - 45</td>
<td>10 – 40</td>
<td>50 – 480</td>
<td>10”</td>
<td></td>
<td>0.01 – 0.055</td>
</tr>
<tr>
<td></td>
<td>Splitview: 18 - 72</td>
<td></td>
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<tr>
<td>E-PVC</td>
<td>100 - 500</td>
<td>50 – 200</td>
<td>50 – 480</td>
<td>10”</td>
<td></td>
<td>0.025 – 0.075</td>
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<tr>
<td></td>
<td>Splitview: 160 - 700</td>
<td></td>
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<td></td>
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<tr>
<td>UP</td>
<td>40 - 100</td>
<td>5 – 30</td>
<td></td>
<td></td>
<td>2 – 3.50</td>
<td>7</td>
</tr>
<tr>
<td>ESRB</td>
<td>170 - 370</td>
<td>150 – 200</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Excludes a potential positive credit of 0 to 0.72 GJ/t for low pressure steam (depending on export possibilities for low pressure steam)

'New' and 'existing' refers to new or existing installations.

** Alternatively, 1 – 12 g/t AOX are achieved for PVC production sites or combined sites with PVC production

Three Member States wanted a split view recorded against the BAT AEL for VCM emissions to air in the production of PVC. The BAT AEL these Member States proposed are shown in the table. The rational for their split view is given as follows: The upper value of the range applies to the small production sites. The wide range of the BAT AEL does not belong to different BAT performance but to different product mix manufacturing. Any BAT AEL in this range is related to plants applying BAT throughout their processes.
7) Concluding remarks

The information exchange on Best Available Techniques for the Production of Polymers was carried out from 2003 to 2005. The information exchange process was successful and a high degree of consensus was reached during and following the final meeting of the Technical Working Group. Only one split view was recorded and this was for the BAT associated emissions levels in PVC production.

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