ORGANIC CHEMICAL INDUSTRY
PVC PRODUCTION BY THE SUSPENSION PROCESS

SYNOPSIS SHEET

Prepared in the frame work of EGTEI
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1. Activity description and EGTEI contribution

In order to estimate costs of NMVOC emission reduction in the organic chemical industry, it was decided to split it into 4 sections and to consider an illustrative example for representing each of these sections [1]. The four sections are as follows:

- The PVC suspension process for representing a production of chemicals with sanitary impact.
- A process of the downstream chemistry for representing production of chemicals except the steam crackers, the PVC production and the speciality chemical industry. This production can be also representative of no sanitary impact unit.
- Production of pharmaceutical active ingredients representing the speciality chemical industry (production in batch processes and multipurpose plants).

In the three first activities NMVOC emissions are due to processes themselves, in the last one NMVOC emissions originate from solvent uses.

This synopsis sheet is related to the PVC production by the suspension process only.

The suspension process for producing PVC resins is characterised by the formation of polymers in droplets of liquid vinyl chloride monomer (VCM) or other co-monomers suspended in water by agitation. Polymerisation starts by adding monomer-soluble initiators, then addition of suspension stabilisers and suspending agents minimises the coalescence of the grains. Polyvinylchloride resin, unreacted VCM (in the water, in the headspace, and trapped in the resin) and water are the constituents remaining in the polymerisation reactor. Generally, this polymer slurry is stripped of unreacted VCM using steam and vacuum. This can be done in the reactor itself or in a separate vessel or column. The unreacted stripped VCM is purified, stored and recycled, and non-condensable gases are vented after treatment.

After stripping, the slurry of PVC containing very low amount of VCM is transferred to blend tanks which mix the batch with other batches to insure product uniformity. The mixed batches are then fed to a continuous centrifuging operation that separates the polymer from the water in the slurry. Both, mixing tanks and centrifuges are vented to the atmosphere. The centrifuge water is recycled back to the process or discharged to the plant's wastewater treatment system after stripping.

The wet cake from centrifuging is conveyed to a dryer for further removal of the remaining (usually 25%) moisture. Drying time is generally short, but large volumes of air are released.

During the PVC suspension production, process emission sources include:
- VCM unloading and storage,
- opening of equipment for cleaning and maintenance,
- process vents, such as blending tank vents, monomer recovery system vents, and dryer exhaust vents,
- equipment leaks from valves, flanges, pumps, compressors, relief devices, sample connections, and open-ended lines,
- other diffuse sources such as gasholders and wastewater.

Most of emission factors from literature are obsolete, due to constant improvement of s-PVC technology and industrial practices. Common values in Western Europe for process emissions are below 100 g/Mg product after 2000 (ECVM Industry Charter for the Production of VCM and PVC – 2000).

This activity emits NMVOC. Most of VOC is VCM. At a EU25 level for the year 2000 (according to the RAINS model: version CP_CLE_Aug04(Nov04)), NMVOC emissions were 15.7 kt representing 0.15% of total NMVOC emissions [8]. These estimations could be modified in a near future due to information delivered by national experts during the bilateral consultation scheduled in 2005.

Organic chemical industry is addressed by the EC Directive 96/61/EC of council of 1996, September 24th related to Integrated Pollution Prevention and Control (IPPC).
The methodology for this sector has been developed on the basis of information provided by an expert group from CEFIC [4].

Organic chemical industry was considered as a unique sector in the previous RAINS version [7]. EGTEI provides a first approach to tackle this complex sector by considering three sub activities in order to better represent costs and abatement scenarios. Data provided by EGTEI, emission factors, efficiencies and costs of reduction techniques are presently used in the new RAINS version for the modelling work carried in the scope of the CAFÉ programme and the revision of the Gothenburg Protocol and national emission ceiling directive.

The representative activity unit used is the annual production of PVC by suspension process expressed in kt/year. Only one reference installation is considered. Four reduction measures based on different combination of reduction techniques such as stripping, vent gas treatment, diffuse and fugitive emission treatment according to EVCM methodologies, closed lid reactor… are considered.

EGTEI provides default emission factors (EF) with abatement efficiencies, investments, variable and fixed operating costs (OC) as well as unit costs expressed in €/t NMVOC and €/kt PVC for the four reduction measures.

Unit costs range from 314 to 1043 €/t NMVOC abated according to the reduction measure considered and from 9.4 to 31.3 €/t PVC. No country specific or country and sector specific parameters are required. National experts have only to provide the trends in activity level from 2000 to 2020 as well as the application and applicability rates of each abatement technique.

As the sector representation in RAINS [8] is presently based on the EGTEI proposal, it is recommended to national experts to complete ECODAT with country specific parameters which are not known from CIAM.

In the future however, any new technology which could be developed should be considered by EGTEI in the background document to continuously improve the sector representation and the EGTEI capacity to describe new technologies.

2. European regulation

Organic chemical industry is addressed by the EC Directive 96/61/EC of council of 1996, September 24th related to Integrated Pollution Prevention and Control (IPPC).

3. Methodology developed within EGTEI to represent the sector

3.1 Definition of the reference installation

The reference unit is a 250 kt/yr plant, at the 1970 stage, consisting of a very basic suspension process, without any stripping or recovery of VOC.

<table>
<thead>
<tr>
<th>Reference Installation Code (RIC)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>250 kt/yr plant, life time : 10 years, Plant factor [h/year] : 8000</td>
</tr>
</tbody>
</table>

3.2 Definition of emission abatement techniques

3.2.1 Primary measures

The losses due to leakage can be limited by uses of certain types of gaskets, flanges, pumps packing and seals, and by use of continuous VCM emissions monitoring. Such modifications have been introduced by the Western Europe s-PVC industry since 1974.
For simplification in the presentation of reduction techniques, they are presented with secondary measures. No primary measures appear in the codification of measures are taken into account.

3.2.2 Secondary measures
The secondary reduction techniques considered are as follows:

- Stripping the residual VCM and vent gas treatment which are the most consistent measures in terms of VOC reduction.
- Diffuse and fugitive emission treatment program according to ECVM methodologies (LDAR-Leak Detection And Repair),
- Optimisation of different emission treatments, most of them in combination, depending the specific process or local conditions (stripping, vent gas, closed lid reactor, closed sampling...)

<table>
<thead>
<tr>
<th>RIC PMC SMC</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>01 00 00</td>
<td>None</td>
</tr>
<tr>
<td>01 00 01</td>
<td>Stripping and vent gas treatment</td>
</tr>
<tr>
<td>01 00 02</td>
<td>01 00 01 + Diffuse and fugitive emissions treatment program according to ECVM methodologies</td>
</tr>
<tr>
<td>01 00 03</td>
<td>01 00 01 + Optimised treatments (stripping, vent gas, closed lid reactor, closed sampling...)</td>
</tr>
<tr>
<td>01 00 04</td>
<td>01 00 03 + Diffuse and fugitive emissions treatment program according to ECVM methodologies</td>
</tr>
</tbody>
</table>

4. Country specific data to be collected
For PVC suspension, costs have been calculated for Europe as a whole as default value. No development has been made for enabling to calculate country specific costs.

Table 4.1: Unabated emission factor [kg NMVOC / t PVC]

<table>
<thead>
<tr>
<th>Default emission factor</th>
<th>Country specific emission factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0</td>
<td>To be provided by national experts</td>
</tr>
</tbody>
</table>

5. Default emission factors and cost data defined with the EGTEI methodology
Table 5.1 presents an overview of all data provided by the EGTEI methodology for the reference installation: default emission factors with abatement efficiencies, investments, variable and fixed operating costs as well as unit costs.

<table>
<thead>
<tr>
<th>RIC PMC SMC</th>
<th>NMVOC EF [g/t PVC]</th>
<th>Abatement efficiency [%]</th>
<th>Investment [k€]</th>
<th>Variable OC [k€/y]</th>
<th>Fixed OC [k€/y]</th>
<th>Unit cost [€/t NMVOC abated]</th>
<th>Unit cost [€/t PVC]</th>
</tr>
</thead>
<tbody>
<tr>
<td>01 00 00</td>
<td>30000</td>
<td>99.68</td>
<td>7700</td>
<td>1200</td>
<td>200</td>
<td>314.3</td>
<td>9.40</td>
</tr>
<tr>
<td>01 00 01</td>
<td>96</td>
<td>99.72</td>
<td>7900</td>
<td>1200</td>
<td>400</td>
<td>344.2</td>
<td>10.30</td>
</tr>
<tr>
<td>01 00 02</td>
<td>83</td>
<td>99.82</td>
<td>42100</td>
<td>1300</td>
<td>1200</td>
<td>1027.2</td>
<td>30.76</td>
</tr>
<tr>
<td>01 00 03</td>
<td>53</td>
<td>99.87</td>
<td>42300</td>
<td>1300</td>
<td>1300</td>
<td>1043.4</td>
<td>31.26</td>
</tr>
</tbody>
</table>
Unit costs increase from the first reduction measure to the most efficient one.

6. Relevance of EGTEI information for integrated assessment modelling (IAM)

In the previous RAINS version [7], the sector ORG PROC represented the organic chemical industry as a whole. Storage of chemical products was considered under sector ORG_STORE.

The module has been modified to take into account the EGTEI proposal. The organic chemical industry has been divided in three sub activities. For PVC production by suspension process (under PVC-PVC_PR) the following reduction techniques are considered. Reduction measure definitions and their efficiencies are based on EGTEI proposals:

- PVC-PVC_PR-STVNT: 99.68%
- PVC-PVC_PR-STVNT+LK: 99.72%
- PVC-PVC_PR-STVNTOPT: 99.82%
- PVC-PVC_PR-STVNTOPT+LK: 99.87%

Data provided in EGTEI approach (emission factors, efficiencies) have been implemented in the new version of the RAINS model [8] for the modelling work carried out in the scope of the CAFÉ programme and the revision of the Gothenburg protocol. Costs are not yet available on the web site.

For this activity now, data provided by national experts through ECODAT can then be directly used by CIAM for introduction in the RAINS model.

7. Perspective for the future

The EGTEI proposal for the representation of PVC production and definitions of abatement techniques has been considered in the last update of RAINS [8].

In fact it could be useful to extend the work to other typical chemical processes to better take into account the specificities of this industry.

8. Bibliography

[1] MONZAIN M. (UIC) ; MONGENET F. (UIC) ; CASTRO F. (UIC): Meeting held in Paris on 21/08/02 with N. ALLEMAND and J. VINCENT from CITEPA aiming at defining the best approach for cost definition in the organic chemical sector. Minutes of the meeting.
[3] Rapport d’inventaire national au format UNECE/NFR et NEC
[4] Expert group from PVC manufacturers : TRIOPOS S. (LVM); LIEGEOIS R. (Solvay); LOUIS H. (Atofina); BINDELLE J.P. (Solvay), DE CHAMPS F. (SPMP).
[8] Review of data used in RAINS-VOC model http://www.iiasa.ac.at/web-apps/tap/RainsWeb/RainsServlet1
[9] CITEPA. National reference centre for emissions inventories
Example of data collection and use of EGTEI data – Case of France

A. Country specific data collection and CLE scenario developed

The French national expert has been able to complete ECODAT for the PVC production with help of CITEPA [9]. All data have been prepared by the French national expert for the bilateral consultations member state – CIAM which ended in March 2004.

Country and sector specific economic parameters

No country and sector specific economic parameters.

Activity level

The increase in activity level from 2000 to 2020 has been provided by SPMP from 2000 to 2010 [10] and is of 1.059 %/year. From 2010 to 2020, the same increase rate than from 2000 to 2010, is taken into account. Activity levels are presented in table A.1.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>125.649</td>
<td>132.45</td>
<td>139.61</td>
<td>147.16</td>
<td>155.12</td>
</tr>
</tbody>
</table>

Unabated emission factor

The French emission factor used is equal to the default emission factor provided by EGTEI.

<table>
<thead>
<tr>
<th></th>
<th>Default unabated emission factor [kg/t PVC]</th>
<th>French unabated emission factor [kg/t PVC]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30.0</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Current legislation control (CLE)

In the current legislation control scenario (CLE), application rates of the different abatement techniques depend on regulation implemented and on dates of compliance required by this regulation but also internal development not driven by regulation.

In 2000, SMC 01 and 03 were in operation according to data provided by industry experts [6], [4]. In the CLE scenario, application rates of reduction techniques from 2005 to 2010 have been defined by industry. It is assumed that application rates in 2015 and 2020 are those of 2010.

Application rates for the current legislation scenario are presented in table A.2.

<table>
<thead>
<tr>
<th></th>
<th>Application rate in 2000 [%]</th>
<th>Application rate in 2005 [%]</th>
<th>Appl. [%]</th>
<th>Application rate in 2010 [%]</th>
<th>Appl. [%]</th>
<th>Application rate in 2015 [%]</th>
<th>Appl. [%]</th>
<th>Application rate in 2020 [%]</th>
<th>Appl. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>01 00 00</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>01 01 00</td>
<td>40</td>
<td>20</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>01 02 00</td>
<td>0</td>
<td>20</td>
<td>100</td>
<td>40</td>
<td>100</td>
<td>40</td>
<td>100</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>01 03 00</td>
<td>60</td>
<td>30</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>01 04 00</td>
<td>0</td>
<td>30</td>
<td>100</td>
<td>60</td>
<td>100</td>
<td>60</td>
<td>100</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>Total RIC 01</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
</tbody>
</table>
B. Trends in emissions and total costs of the CLE scenario

Table B.1 presents the trends in NMVOC emissions from 2000 to 2020 according to the CLE scenario and associated total annual costs (Data presented in the table B.1 are directly provided by ECODAT and based on input parameters defined in chapter A).

Table B.1: trends in emissions and total annual costs of emission reductions in the CLE scenario

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NMVOC emissions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CLE scenario</td>
<td>8.8</td>
<td>8.4</td>
<td>8.0</td>
<td>8.4</td>
<td>8.9</td>
</tr>
<tr>
<td><strong>Total annual costs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CLE scenario</td>
<td>2791</td>
<td>2986</td>
<td>3194</td>
<td>3366</td>
<td>3548</td>
</tr>
</tbody>
</table>