ORGANIC CHEMICAL INDUSTRY
STEAM CRACKING

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 steam cracking process with naphtha as feedstock and ethylene and propylene as products is considered as the illustrative example taken into account for representing all the production of lower olefins (ethylene, propylene, butanes and butadienes). Within the EC, there are 50 steam crackers and these are located on 39 sites [2].
- 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 steam cracking only.

Steam cracking units are complex installations in which suitable hydrocarbons (naphtha, gas-oil…) are heated to very high temperatures, in the presence of steam, to split the molecules into olefins of lower molecular weigh such as unsaturated hydrocarbons: ethylene, propylene, butanes, butadienes. An excellent description of the process is given in the BREF document on large volume organic compounds [2].

Olefin plants are part of integrated petrochemical and/or refining complex. Common utilities are provided by central facilities. It is very difficult to compare emissions from unit to unit since plant boundary definitions and degree of integration of each plant are different. All or part of the storage facilities for example can be present depending on the production structure and connexions with upstream and downstream units. Moreover, estimation of emissions is a difficult issue in this activity and methodologies used from plant to plant, country to country are not the same.

Different feed stocks produce different ethylene and propylene yields and ranges of products. When naphtha is used, ethylene and propylene represent 45 % of the product yields (other products are for example methane, propane, ethane, acetylene, butadiene, butylenes…) [4].

NMVOC emissions result from:

- Stack emissions
- Diffuse emissions from storages of raw materials, storages of final products, loading and unloading operations and waste water treatment plants
- Fugitive emissions.

Diffuse emissions are not addressed in the background document. Only fugitive and stack emissions are addressed.

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 prepared on the basis of information provided by an expert group from UIC and CEFIC [4], [5].

This activity emits NMVOC. At a EU25 level for the year 2000 (according to RAINS: version CP_CLE_Aug04(Nov04)), NMVOC emissions were 83 kt representing 0.78% of total NMVOC emissions [10]. The resulting emission factor, just lower than 3 kg NMVOC / t ethylene+propylene indicates a low use of reduction techniques in 2000. 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 was considered as a unique sector in the previous RAINS version [9]. EGTEI provides a first approach to tackle this complex sector by considering three sub activities in order to better represent costs and abatement scenarios (the speciality organic chemistry being already considered in RAINS). Data provided by EGTEI, emission factors, efficiencies and costs of reduction techniques are presently used in the new RAINS version [10] 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 ethylene and propylene (E+P) expressed in kt/year. Only one reference installation is considered.

Four primary measures based on different leak and detection and repair programme (LDAR) are considered. In some Member states such programmes are mandatory.

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 E+P for the four reduction measures.

Unit costs range from -96 to + 178 €/t NMVOC abated according to the reduction measure considered and from -147 to 335 €/kt E+P. Negative costs indicate that savings are high and counter balance investment and operating costs.

National experts have to collect only one country specific parameter (wage costs) and one country and sector specific parameters (naptha costs). These parameters can be very easily known through the chemical industry associations. National experts have also 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 [10] 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. It should be necessary to review the considered efficiencies regularly to update them and perhaps define an additional reduction technique if necessary.

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### 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). No direct emission limit value is introduced in this directive. Nevertheless permit emission limit values have to be based on BAT performances.

### 3. Methodology developed within EGTEI to represent the sector

#### 3.1 Definition of the reference installation

From data collected by UIC at the French level [4] and CEFIC at European level, a reference installation defined as a steam cracker with a capacity of 480 000 t of ethylene (the leading output of the cracker) and 270 000 t of propylene and naphtha as feedstock (the largest feedstock used) has been taken into account.

Stack VOC emissions from the cracking process can be assumed to be recycled at a maximum level into the process or used as a fuel or routed to associated processes. Its total emissions are about 50 t.

As said above, the boundaries of the reference installation taken into account for estimating costs of reduction measures, exclude diffuse emissions from storages and loading/unloading operations.

On average according to UIC, this installation has about 50 000 potentially leaking points (valves, flanges, pumps, open ends…) of which 40 000 are accessible for control and repair. In the scope of this study, a simplified installation with 50 % valves and 50 % flanges is considered.
Table 3.1.1: Definition of the reference installation

<table>
<thead>
<tr>
<th>Reference Installation Code (RIC)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Steam cracker unit with a capacity of 480 kt of ethylene + 270 kt propylene and naphtha as feed stock. Elevated flare systems with efficiency of 99.5%, VOC emissions: 30 t/yr. Other stack VOC emissions from the cracking process recycled into the process, used as a fuel or routed to associated processes and maintained as low as possible. Stack VOC emissions: 20 t/yr. Without measure, total VOC emissions are 2500 t (other emissions come from storage and waste water treatment plant)</td>
</tr>
<tr>
<td>50 000 potentially leaking points (valves, pumps, flanges, open ends…); 40 000 accessible points: 50 % valves and 50 % flanges.</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Definition of emission abatement techniques

3.2.1 Primary measures

Fugitive emissions can be reduced through a Leak Detection And Repair programme (LDAR) [6].

A LDAR programme aims at detecting (or screening which is a measure of the concentration of leaking compounds in the ambient around an equipment piece air that provides an indication of the leak rate from this equipment piece, measured in units of parts per million by volume (ppmv)) and repairing equipment that is identified as leaking. The LDAR programme efficiency depends on how a leak is defined for repairing actions, types of repairing actions carried out (tightening, simple replacement of the leaking equipment, replacement with the highest standard of equipment not leaking any more), final leak frequency after the LDAR programme has been implemented.

A LDAR programme is established according to the following principles:

- 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 on the leak category.

Repair procedures related to leak category considered in primary measures are indicated in table 3.2.1.1.

4 LDAR programmes are considered for the estimation of costs. They differ from the level of leak considered and type of maintenance carried out.

Table 3.2.1.1: Abatement measures considered

<table>
<thead>
<tr>
<th>Primary Measure Code PMC</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>00</td>
<td>No LDAR programme</td>
</tr>
<tr>
<td>01</td>
<td>Establishment of the LDAR programme&lt;br&gt;Inventory of all components and establishment of a database.&lt;br&gt;First screening of all potential leak points of the plant (100 % of accessible points are considered and controlled), analysis of the first results of the survey.&lt;br&gt;Tightening for points &gt; 5 000 ppm&lt;br&gt;Basic maintenance for 100 % points &gt; 100 000 ppm during first shut down.&lt;br&gt;Annual control between two shutdowns&lt;br&gt;Intermediate campaign before shutdown: 20 % of accessible points are controlled each year (in five years all points are controlled).&lt;br&gt;Tightening each year for 100 % controlled points &gt; 5 000 ppm.&lt;br&gt;Next Shutdown.&lt;br&gt;Basic maintenance for 100 % measured points (during the 5 years) &gt; 100 000 ppm.</td>
</tr>
</tbody>
</table>
Establishment of the LDAR programme
Inventory of all components and establishment of a database.
First screening of all potential leak points of the plant (100% of accessible points are considered and controlled), analysis of the first results of the survey.
Tightening for points > 1000 ppm.
Basic maintenance for points > 10 000 ppm during the first shut down.
Annual control between two shutdowns
Intermediate campaign before shutdown: 20% of accessible points are controlled each year (in five years all points are controlled).
Tightening each year for 100% controlled points > 1 000 ppm.
Next Shutdown
Basic maintenance for 100% measured points (during the 5 years) > 10 000 ppm.

Establishment of the LDAR programme
Inventory of all components and establishment of a database.
First screening of all potential leak points of the plant (100% of accessible points are considered and controlled), analysis of the first results of the survey.
Tightening for points > 1000 ppm.
Basic maintenance for 100% points > 5 000 ppm during the first shut down.
Annual control between two shutdowns
Intermediate campaign before shutdown: 20% of accessible points are controlled each year (in five years all points are controlled).
Tightening each year for 100% measured points > 1 000 ppm.
Next Shutdown
Basic maintenance for 100% measured points (during the 5 years) > 5 000 ppm.

Establishment of the LDAR programme
Inventory of all components and establishment of a database.
First screening of all potential leak points of the plant (100% of accessible points are considered and controlled), analysis of the first results of the survey.
Tightening for points > 1 000 ppm.
Basic maintenance for flanges points >10000 ppm during the first shut down.
Heavy maintenance for valves points > 10 000 ppm during the first shut down.
Annual control between two shutdowns
Intermediate campaign before shutdown: 20% of accessible points are controlled each year (in five years all points are controlled).
Tightening each year for points > 1 000 ppm.
Next Shutdown
Basic maintenance for 100% measured (during the 5 years) > 10 000 ppm.
Heavy maintenance for 100% measured (during the 5 years) > 10 000 ppm.

3.2.2 Secondary measures
No secondary measure has been taken into account.

4. Country specific data to be collected
Different types of country specific data have to be collected to give a clear picture of the situation in each Party. EGTEI proposes default values for these economical parameters which can be modified by the national expert if better data are available.
For steam cracking, only one country and sector specific economic parameter and one country specific economic parameter are required. They are presented in tables 4.1 and 4.2 as the default costs proposed by EGTEI for this activity.

Table 4.1: Country specific economic parameter cost

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Default cost provided by EGTEI</th>
<th>Country specific cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wages [€/h]</td>
<td>24.3</td>
<td>to be provided by national experts</td>
</tr>
</tbody>
</table>
Table 4.2: Activity and country specific parameter cost

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Default cost provided by EGTEI</th>
<th>Country specific cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphtha cost €/t (main feedstock used)</td>
<td>200</td>
<td>to be provided by national experts</td>
</tr>
</tbody>
</table>

Information concerning activity levels from 2000 to 2020 as well as the description of the control strategy is also necessary (these data can be directly entered in ECODAT). A full definition of the work to be done by national experts is provided in the general EGTEI methodology [7].

The national expert can also modify the default unabated emission factor proposed by EGTEI to represent the reference situation of the steam cracking for all Parties in a range of ± 10% (with appropriate explanations).

Table 4.3: Unabated emission factor [kg NMVOC / t Ethylene + Propylene]

<table>
<thead>
<tr>
<th>Default emission factor</th>
<th>Country specific emission factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4</td>
<td>To be provided by national experts</td>
</tr>
</tbody>
</table>

Remark: For this activity, a simple method has been used in ECODAT to estimate costs. In fact for the time being to avoid complex computer programme, only default values can be used. For estimating country specific costs, the EXCEL sheet has to be used.

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 the cost efficiency and unit costs.

Table 5.1: Emission factors (EF), abatement efficiencies, investments and operating costs (OC), unit costs for each combination

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>01 00 00</td>
<td>0.340</td>
<td>0.87</td>
<td>45.0</td>
<td>445 000</td>
<td>64 020</td>
<td>229 450</td>
<td>-96</td>
<td>-147</td>
<td></td>
</tr>
<tr>
<td>01 01 00</td>
<td>1.65</td>
<td>51.5</td>
<td>660 000</td>
<td>94 330</td>
<td>262 430</td>
<td>-66</td>
<td>-115</td>
<td></td>
<td></td>
</tr>
<tr>
<td>01 02 00</td>
<td>1.56</td>
<td>54.1</td>
<td>900 000</td>
<td>127 130</td>
<td>276 090</td>
<td>-28</td>
<td>-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>01 03 00</td>
<td>1.52</td>
<td>55.3</td>
<td>2 100 000</td>
<td>275 110</td>
<td>282 350</td>
<td>178</td>
<td>335</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

E+P: Ethylene + propylene

Negative annual costs means that LDAR programme cost is counter balanced by product saving.

It has to be kept in mind that NMVOC fugitive emissions depend on the method used for estimating them. EGTEI data are based on the use of EPA 21 method considering only generic correlations provided by EPA (the use of specific correlations could give lower emissions). The use of other types of estimation methods could give other costs.

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

In the previous version of the RAINS model [9], 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 (“pharma” already represent the speciality organic chemistry). For steam cracking (under EP-STCRACK-PR) the following reduction techniques are considered.
Reduction measure definitions and their efficiencies are based on EGTEI proposals:

- EP-STCRACK-PR-LDARI: 45%
- EP-STCRACK-PR-LDARII: 51.5%
- EP-STCRACK-PR-LDARIII: 54.1%
- EP-STCRACK-PR-LDARIV: 55.3%

Data provided in EGTEI approach (emission factors) have been implemented in the new RAINS version [10] 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. According to information received from Z. Klimont, investment costs in RAINS are defined slightly differently from EGTEI but just in order to remove labour costs from investments. Annualized investment costs and operating costs are consistent with EGTEI data.

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 chemical industry representation in three sub sectors (steam cracking, PVC production by the suspension process and downstream units) and definitions of abatement techniques has been considered in the last update of RAINS [10].

NMVOC emissions mainly occur from leak on equipment. Monitoring of fugitive emissions is a very new activity. It should be interesting to update emission factors with results of monitoring which could be carried out in Europe mainly in countries where regulations have been implemented. It should be also necessary to update costs and for this, new experience in industry could be used.

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


[5] MONZAIN M. (UIC) ; DE MOULIN J.M. (CEFIC); HARSHAM K. (CEFIC) ; MARLIER G. (UIC) ; SCOLES G. (Shell chemicals) ; : Meeting held in Paris on 13/03/03 with N. ALLEMAND from CITEPA for the cost definition in steam cracking. Minutes of the meeting.


[7] Egtei methodology


Example of data collection and use of EGTEI data – Case of France

A. Country specific data collection and scenario CLE developed
The French national expert has been able to complete ECODAT for steam cracking with help of CITEPA [11] and consultation of UIC [4]. All data have been prepared by the French national expert for bilateral consultations member state – CIAM which ended in March 2004.

Country and sector specific parameters
Cost for country specific economic parameter is has follows

<p>| Table A.1: Country specific economic parameter cost |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>French specific cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wages [€/h]</td>
<td>23.4</td>
</tr>
</tbody>
</table>

Naphta cost has to be provided.

<p>| Table A.2: Activity and country specific economic parameter cost |</p>
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Default cost provided by EGTEI</th>
<th>French specific cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>naphtha cost [€ (net of taxes)/t (main feedstock used)]</td>
<td>200</td>
<td>200</td>
</tr>
</tbody>
</table>

Activity level
The activity level from 2000 to 2020 is kept constant even if a slight production increase is expected. This is due to the fact that fugitive emissions are more related to the number of steam crackers and number of potentially leaking points than to the production level.

| Table A.3: Activity level on the reference Installation (kt Ethylene + Propylene / year) |
|-----|------|------|------|------|------|
| 01  | 5350 | 5350 | 5350 | 5350 | 5350 |

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

<p>| Table A.4: Unabated emission factor |</p>
<table>
<thead>
<tr>
<th>Default unabated emission factor [kg/t Ethylene + Propylene]</th>
<th>French unabated emission factor [kg/t Ethylene + Propylene]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Current legislation control (CLE) scenario
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 the CLE scenario, reduction technique application rates from 2005 to 2020 have been defined considering the requirement for compliance with the French regulation for this type of application (Circulaire of November 23rd, 2004). NMVOC limits are implemented for this activity. The compliance date for existing installations is October 2005. In October 2005, all installations are not in compliance yet. This has been taken into account (application rate lower than 100 for measure 01 or 02) Application rates for the current legislation scenario are presented in table A.5.
Table A.5: Application rates and applicability for each combination of reduction measures in the CLE scenario

<table>
<thead>
<tr>
<th>RIC PMC SMC</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>100</td>
<td>50</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>0</td>
<td>50</td>
<td>100</td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>50</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>01 02 00</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>50</td>
<td>100</td>
<td>50</td>
<td>100</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>01 03 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 04 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>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 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>NMVOC emissions</td>
<td>t COV</td>
<td>t COV</td>
<td>t COV</td>
<td>t COV</td>
<td>t COV</td>
</tr>
<tr>
<td>CLE scenario</td>
<td>18190</td>
<td>14097</td>
<td>9416</td>
<td>9416</td>
<td>9416</td>
</tr>
<tr>
<td>Total annual costs</td>
<td>k€/year</td>
<td>k€/year</td>
<td>k€/year</td>
<td>k€/year</td>
<td>k€/year</td>
</tr>
<tr>
<td>CLE scenario</td>
<td>0</td>
<td>-408</td>
<td>-737</td>
<td>-737</td>
<td>-737</td>
</tr>
</tbody>
</table>

EGTEI approach allows representing NMVOC emissions from steam cracking very well. With EGTEI methodology, emissions estimated in 2000 with the CLE scenario are totally consistent with what is provided by the French emission inventory [3].