Methodology for the free allocation of emission allowances in the EU ETS post 2012

Sector report for the chemical industry

November 2009

Ecofys (project leader)
Fraunhofer Institute for Systems and Innovation Research
Öko-Institut

By order of the European Commission

Study Contract: 07.0307/2008/515770/ETU/C2
Ecofys project Number: PECSNL082164

Disclaimer and acknowledgements

Disclaimer

The views expressed in this study represent only the views of the authors and not those of the European Commission. The focus of this study is on preparing a first blueprint of an allocation methodology for free allocation of emission allowances under the EU Emission Trading Scheme for the period 2013 – 2020 for installations in the refinery industry. The report should be read in conjunction with the report on the project approach and general issues. This sector report has been written by the Fraunhofer Institute for Systems and Innovation Research.

Acknowledgements

The authors would like to thank representatives from the chemical industry for the in-depth discussions on possible benchmarking options for the chemical industry during the execution of the project.

Table of contents

1 Introduction

The Chemical Industry produces many different products. In the context of the new chemical regulation REACH the “European Chemical Agency” gets pre-registrations for 150000 different substances from 65000 companies in 2008 (ECHA 2008).

Out of these substances only a few are explicitly mentioned in the amended Directive[1]. The following table shows the activities named in Annex I to the amended Directive and the corresponding NACE codes.

Table 1 Chemical activities named in Annex I to the amended Directive and corresponding NACE codes

No.	Annex I category of activities	NACE code (Rev. 1.1)	Description NACE
1	Production of carbon black involving the carbonisation of organic substances such as oils, cracker and destillation residues, where combustion units with a total rated thermal input exceeding 20 MW are operated	2413	Manufacture of other inorganic basic chemicals
2	Production of nitric acid	2415	Manufacture of fertilisers and nitrogen compounds
3	Production of adipic acid	2414	Manufacture of other organic basic chemicals
4	Production of glyoxal and glyoxylic acid	2414	Manufacture of other organic basic chemicals
5	Production of ammonia	2415	Manufacture of fertilisers and nitrogen compounds
6	Production of bulk organic chemicals by cracking, reforming, partial or full oxidation or by similar processes, with a production capacity exceeding 100 t per day	2414, (2416), (2417)	Manufacture of other organic basic chemicals (Manufacture of plastics and synthetic rubber in primary forms)
7	Production of hydrogen (H_2) and synthesis gas by reforming or partial oxidation with a production capacity exceeding 25 t per day	2411	Manufacture of industrial gases
8	Production of soda ash (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$)	2413	Manufacture of other inorganc basic chemicals

All activities can be connected to a NACE code. Most activities are explicitly included via a product definition in Annex I to the amended Directive (e.g. production of carbon black, nitric acid), but number 6 of the listed activities is a bit more ambiguous. The phrasing “Production of bulk organic chemicals... by similar processes, with a production capacity exceeding 100 t per day” leads, according to the Association of Petrochemical Producers in Europe (APPE), to the inclusion of further 25 petrochemicals in the ETS.

---

[1] Directive 2009/29/EC amending Directive 2003/87/EC

Table 2 Petrochemicals possibly to be benchmarked according to APPE (APPE 2009a)

1 Ethylene / Propylene
2 Aromatics
3 Cyclohexane
4 Aniline (incl. Nitrobenzene)
5 p-Xylenes
6 Terephthalic acid / Dimethyltryptamine
7 Butadiene
8 Polyethylene
9 Polypropylene
10 Polystyrene
11 Polyvinylchloride
12 Ethylene oxide
13 Monoethylene glycol
14 Vinyl chloride (incl. Ethylene dichloride)
15 Styrene (incl. Ethylbenzene)
16 Akrylnitril
17 Cumene
18 Phenol
19 Acetone
20 Propylene oxide
21 2-Ethylhexanol
22 Polyethylene terephthalate
23 Caprolactam
24 Ethylene propylene diene M-class rubber
25 Acrylic acid

The reason why APPE includes the 25 petrochemicals in the EU ETS is that according to their definition the 25 petrochemicals are bulk organic chemicals being produced in installations with a production capacity exceeding 100 t per day. The 25 petrochemicals do not all belong to the sector group 2014 (Manufacture of other organic base chemicals) but also to the groups 2016 and 2017 (Manufacture of plastics and synthetic rubber in primary forms). The production criteria may be fulfilled, but it is questionable whether a process like polymerisation may be understood as a “similar process” compared to cracking or reforming. Concerning this the Annex I phrasing is ambiguous and can be interpreted in different ways.

Furthermore, many production processes in the chemical industry consume steam (most of the petrochemicals mentioned above) which is produced in installations combusting fuels (exceeding 20 MW) and therefore are included in the EU ETS. This results in much more products in the EU ETS than explicitly named in Annex I to the amended Directive.

In phase I (2005-2007) no chemical products were explicitly named in Annex I of the amended Directive. However, steam production, which is common in the chemical industry, was included from 2005 since steam is produced in “combustion installations with a rated thermal input exceeding 20 MW”. In phase II (2008-2012) production sites producing ethylene and propylene (steam crackers) with a production capacity exceeding 50000 t per year and combustion plants producing carbon black with a thermal input exceeding 20 MW have been included.

2 Production processes GHG emissions – approach towards benchmarking the sector

The chemical industry being represented by Cefic (European Chemical Industry Council) has indicated three different options to benchmark processes in the chemical industry (CEFIC 2009a):

1. In the first approach, processes are covered with benchmarks for direct process emissions are indicated by the 80/20 principle. This means that processes being responsible for 80% of the total emissions of the chemical industry are covered by product benchmarks, for the remaining 20% a fall-back approach is used (see section 5 of the report on the project approach and general issues).
2. The second option is similar to the first approach. However, within the 80% steam is not considered to be an own product, but the emissions emerging from the production of steam are counted to the process emissions and therefore the efficiency of steam consumption is accounted for. For the remaining 20% a fall-back approach is used
3. The third approach is the most elaborated one and allows for setting up explicit benchmarks for all chemical processes within the EU ETS. In order to cover all different uses of heat within the chemical sector, several hundreds of benchmarks would be required.

The third approach is due to the high number of benchmarks not realistic. The effort to develop several hundred benchmarks is too extensive so that this approach may be regarded as not feasible.

In line with the general approach followed in this project (chapter 4.4.1 in the report on the project approach and general issues), we apply the second approach for benchmarking the chemical sector. In this way, the emissions being released by the steam production are counted to the direct emissions which results in benchmarking the overall efficiency of the products concerned.

For the remaining 20% of the emissions, the fall-back approaches as outlined in chapter 5 of the report on the project approach and general issues are proposed. The following table illustrates the 80/20 principle by showing the most emission intensive activities ranked according to their greenhouse gas emission intensity:

Table 3 Ranking of the most emission intensive activities in the chemical industry (CEFIC 2009b)

No.	Product / process[1]	Process and steam emissions [Mt CO_2-equivalents]	Share	Cumulative share
1	Nitric Acid	41 [4]	21.6%	21.6%
2	Cracker products (HVC)	35	18.4%	40.0%
3	Ammonia	30	15.8%	55.8%
4	Adipic acid	13 [4]	6.8%	62.6%
5	Hydrogen / Syngas (incl. Methanol) [2]	12.6	6.6%	69.3%
6	Soda ash	10	5.3%	74.5%
7	Aromatics (BTX)	6.6	3.5%	78.0%
8	Carbon black	4.6	2.4%	80.4%
9	Ethylene dichloride / Vinyl chloride / PVC	4	2.1%	82.5%
10	Ethylbenzene / Styrene	3.6	1.9%	84.4%
11	Ethylene oxide / Monoethylene glycol	3.6	1.9%	86.3%
12	Cumene / phenol / acetone	1.2	0.6%	86.9%
13	Glyoxal / glyoxylic acid [3]	0.4 [4]	0.2%	87.2%
14	*Polyolefins (PE / PP / PS)*	1.1	0.6%	87.7%
15	*Butadiene*	0.6	0.3%	88.1%
16	*Dimethyl therephthalate / Terephthalic acid / Polyethylene terephthalate*	0.6	0.3%	88.4%
17	*Propylene oxide*	0.5	0.3%	88.6%
18	Others		11.4%	100.0%
	Total upper processes (1-18)	**168.4**	**88.6%**	
	Total chemical industry [5]	**190**	**100.0%**	

[1] In italics, production processes with steam consumption only. Other emissions have direct emission from the process and emissions from steam consumption

[2] This figure includes 3.8 Mt CO_2 from gas producers, who supply refineries. Hydrogen production in refineries accounts for 44 Mt CO_2.

[3] This figure is based on the Registre Français des Emissions Polluantes (IREP), year 2005

[5] Carbon dioxide and nitrous oxide

[5] This figure includes N_2O and CO_2 emissions phrased as Mt CO_2-equivalents and is based on the greenhouse gas inventory, see table 4

The table shows both the absolute figures for the CO_2-equivalent (CO_2 and N_2O emissions) of the activities and the share of those emissions in the total CO_2 and N_2O emissions of the chemical industry in the EU. It should be noted that N_2O emissions are generated only from the production of nitric acid, adipic acid and glyoxal / glyoxylic acid while direct and / or CO_2 emissions related to steam are generated from the production of all products. Using the second approach and deriving the number of product benchmarks from the 80/20 principle there are 8 chemicals whose production accounts for 80% of the N_2O and CO_2 emissions of the chemical industry in the EU:

- Nitric acid
- Cracker products
- Ammonia
- Adipic acid

- Hydrogen / Synthesis gas
- Soda ash
- Aromatics
- Carbon black

We discuss benchmarking for these eight activities in Chapter 3 to 10. Many of the eight activities have direct emissions and consume steam. Since glyoxal / glyoxalic acid is mentioned in Annex I to the amended Directive, this chemical product is described in Chapter 11, although, according to its position in Table 3, a fall-back approach is suggested to be applied to allocate allowances for this product (see section 5 of the report on the project approach and general issues).

Cefic advocates benchmarking for further four production chains (CEFIC 2009c):

- Ethylene dichloride / Vinyl chloride / PVC
- Ethylbenzene / Styrene
- Ethylene oxide / Monoethylene glycol
- Cumene / phenol / acetone

Since Cefic has already started working on benchmarking those products and the 80/20 principle is rather a guideline proposal than a strict prescription, the consortium considers those products also for benchmarking and we gather some first information on them in appendix A. It should be noted, however, that work on these benchmarks is far from completed and no clear methodology can yet be suggested, e.g. with respect to the multiple products that are produced in each of the product chains indicated.

Furthermore, the total emissions of the chemical industry vary from year to year. The estimated 190 Mt used in the ranking belong to the upper level. Normally the total emissions are lower than 190 Mt (see Table 4).

Table 4 GHG emissions of the chemical sector from 2002 to 2007 (EEA 2009)

	2002	**2003**	**2004**	**2005**	**2006**	**2007**	**Average**
CO_2 and N_2O emissions in the chemical sector [Mt CO_2-eq.][1]	174.3	187.7	190.3	195.7	177.0	180.6	184.3

[1] Calculated from the classifications 1.A.2.C, 2.A.4, 2.B. and 3.C. of the GHG inventories

3 Nitric acid

3.1 Production process

The nitric acid production is with a share of 21% at present the largest source of CO_2 / N_2O emissions in the European chemical industry. According to Table 3 in Chapter 2, European nitric acid installations accounted for 41 Mt CO_2-equivalents in 2006.

The following table lists all nitric acid plants in Europe with the corresponding operators and locations. Capacities and site-specific N_2O emissions are not available for all plants.

Table 5 Europe installations for nitric acid: production, capacities and N_2O emission are given according to the reference document on BAT (EFMA 2009a)

	Company	Location	Country	Capacity [t/y]	Capacity [t/d]	kg N_2O / t 100% HNO_3
1	Agro Linz Melamin GmbH	Linz	Austria	300000		0.12 - 0.25
2	Agro Linz Melamin GmbH	Linz	Austria	18000		3.4 - 4.9
3	BASF Antwerpen	Antwerpen	Belgium		1890	
4	BASF Antwerpen	Antwerpen	Belgium		650	
5	BASF Antwerpen	Antwerpen	Belgium			
6	BASF Antwerpen	Antwerpen	Belgium			
7	Yara, Tertre (Be)	Tertre (Hainaut)	Belgium		750	7.2
8	Yara, Tertre (Be)	Tertre (Hainaut)	Belgium		550	7.1
9	Yara, Tertre (Be)	Tertre (Hainaut)	Belgium		850	0.2
10	Agrobiochim	Stara Zagora	Bulgaria			
11	Agropolychim	Devnya	Bulgaria		1100	5.3
12	Neochim	Dimitrovgrad	Bulgaria			
13	Petrokemija	Kutina	Croatia			
14	Lovochemie AS	Lovosice	Czech Rep.	300000		5.5
15	Lovochemie AS	Lovosice	Czech Rep.			
16	Vychodoceske Chem.Zavody Synthesia	Pardubice-Semtin	Czech Rep.			
17	Yara	Uusikaupunki 2 incl. vrm IFI	Finland			
18	Yara	Uusikaupunki 2 incl. vrm IFI	Finland			
19	Yara	Siilinjaervi (Kuopio)	Finland			
20	GPN , Rouen (Fr)	Grand-Quevilly (Rouen)	France			
21	GPN , Rouen (Fr)	Grand-Quevilly (Rouen)	France			
22	GPN , Rouen (Fr)	Grand-Quevilly (Rouen)	France			
23	GPN	Mazingarbe	France			
24	GPN	Mazingarbe	France			

Continuation Table 5

	Company	Location	Country	Capacity [t/y]	Capacity [t/d]	kg N_2O / t 100% HNO_3
25	Pec-Rhin, Mulhouse (Fr) 50% GPN / 50% Yara	Ottmarsheim	France			
26	France	Oissel	France			
27	Gde.Paroisse Nangis	Grandpuits (Nangis)	France			
28	Rhone-Poulenc Chimie	Mulhouse / Chelampe	France			
29	Rhone-Poulenc Chimie	Roussillon	France			
30	Rhone-Poulenc Chimie	Saint Fons	France			
31	Yara	Ambes (Gironde) / Bordeaux	France			
32	Yara	Montoir de Bretagne (Loire Atlantique)	France			
33	Yara , Pardies (Fr)	Pardies (Pyrenees Atlantique)	France			
34	Yara	Rostock	Germany			
35	BASF, Ludwigshafen	Ludwigshafen	Germany			
36	BASF, Ludwigshafen	Ludwigshafen	Germany			
37	BASF, Ludwigshafen	Ludwigshafen	Germany			
38	BASF, Ludwigshafen	Ludwigshafen	Germany			
39	BASF, Ludwigshafen	Ludwigshafen	Germany			
40	BASF, Ludwigshafen	Ludwigshafen	Germany			
41	BP, Koln	Koln	Germany			
42	BP, Koln	Koln	Germany			
43	Kali und Salz	Krefeld	Germany	1500		
44	Petrolchemie u. Kraftstoffe	Schwedt	Germany			
45	Ruhr Oel GmbH	Gelsenkirchen	Germany			
46	SKW Piesteritz	Piesteritz	Germany			
47	PFI , Kavalla (Gr)	NEA Karvali / Kavalia	Greece			
48	Aeval SA	Ptolemais Kozanis	Greece			
49	Pet Nitrogenmuvek Ltd	Petfuerdoe / varpalota	Hungary			
50	Yara	Ravenna Emilia-Romagna	Italy			
51	Enichem	Porto-Marghera-S	Italy			
52	Yara, Nera Montoro (It)	Nera Montoro / Umbria	Italy			
53	Yara Terni	Terni	Italy			
54	Achema JSC	Jonava UKL7 1,2,3,	Lithuania			
55	Achema JSC	Jonava UKL7 4	Lithuania			
56	Achema JSC	Jonava UKL7 5	Lithuania			
57	Achema JSC	Jonava UKL7 6	Lithuania			
58	Achema JSC	Jonava UKL7 ,7	Lithuania			
59	Achema JSC	Jonava UKL7 ,8	Lithuania			
60	Achema JSC	Jonava GP	Lithuania			
61	DSM	Geleen	Netherlands	500000		9.0
62	DSM	Geleen	Netherlands	210000		7.1

Continuation Table 5

	Company	Location	Country	Capacity [t/y]	Capacity [t/d]	kg N_2O / t 100% HNO_3
63	DSM	IJmuiden	Netherlands	255000		5.7
64	DSM	IJmuiden	Netherlands	245000		9.0
65	Yara, Sluiskil	Sluiskil	Netherlands			
66	Yara, Sluiskil	Sluiskil	Netherlands			
67	Yara	Glomfjord	Norway			
68	Yara	Glomfjord	Norway			
69	Yara, Porsgrunn (No)	Porsgrunn	Norway			
70	Yara, Porsgrunn (No)	Porsgrunn	Norway			
71	Yara, Porsgrunn (No)	Porsgrunn	Norway			
72	Zaklady Azotowe (ZAK)	Kedzierzyn	Poland			
73	Zaklady Azotowe (ZAT)	Tarnow	Poland			
74	Zaklady Azotowe Anwil AG (ZAW)	Wloclawek	Poland			
75	Zaklady Azotowe (ZAP)	Pulawy	Poland			
76	AdP	Alverca do Ribatejo	Portugal	126000		
77	Adubos de Portugal SA (Quimigal)	Barreiro	Portugal			
78	Adubos de Portugal SA (Quimigal)	Lavradio	Portugal		360	
79	Adubos de Portugal SA (Quimigal)	Estarrejo	Portugal			
80	Azomures	Targu Mures	Romania			
81	Azomures	Targu Mures	Romania			
82	Azomures	Targu Mures	Romania			
83	Amonil	Slobozia	Romania			
84	doljchim	Craiova	Romania			
85	doljchim	Craiova	Romania			
86	turnu magurele	Turnu Magurele	Romania			
87	turnu magurele	Turnu Magurele	Romania			
88	Azochim	Savinesti	Romania			
89	HIP Azotara PANCEVO	Pancevo	Serbia			
90	HIP Azotara PANCEVO	Pancevo	Serbia			
91	HIP Azotara PANCEVO	Pancevo	Serbia			
92	Chemko Strazske	Strazske	Slovakia			
93	Duslo Chem. Zavody	Sala Nad Vahom	Slovakia			
94	Fertiberia	Aviles	Spain			
95	Fertiberia Puertollano	Puertollano	Spain			
96	Fertiberia Sagunto	Sagunto	Spain			
97	Fertiberia Luchana-B	Luchana-Baracaldo	Spain			
98	Erkimia SA	Tarragona	Spain			
99	Dyno Nitrogen	Ljungaverk	Sweden			
100	Yara	Landskrona (Malmohus)	Sweden			
101	Yara	Koeping (Vastmanland)	Sweden	105000		
102	Yara	Koeping (Vastmanland)	Sweden	136500		

Continuation Table 5

	Company	Location	Country	Capacity [t/y]	Capacity [t/d]	kg N_2O / t 100% HNO_3
103	Lonza AG	Visp	Switzerland			
104	Du Pont (UK) Ltd	Wilton	United Kingdom			
105	Imperial Chemical Industries ICI	Stevenson (Scotland)	United Kingdom			
106	Grow How UK ltd, Ince (UK)	Ince Marshes (Cheshire)	United Kingdom			
107	Grow How UK ltd (UK)	Ince Marshes (Cheshire)	United Kingdom			
108	RGrowHowal Ordnance Division of Lambson Fine Chemicals	Bridgewater	United Kingdom			
109	Richardsons Fertilizers	Belfast	United Kingdom			
110	Grow How UK ltd Billingham	Billingham	United Kingdom			
111	Grow How UK ltd Billingham	Billingham	United Kingdom			
112	Grow How UK ltd Billingham	Billingham	United Kingdom			
113	Grow How UK ltd Billingham	Billingham	United Kingdom			
114	Grow How UK ltd Severnside	Redwick Severnside (Bristol)	United Kingdom			
115	Grow How UK ltd Severnside	Redwick Severnside (Bristol)	United Kingdom			
92	Chemko Strazske	Strazske	Slovakia			
93	Duslo Chem. Zavody	Sala Nad Vahom	Slovakia			
94	Fertiberia	Aviles	Spain			
95	Fertiberia Puertollano	Puertollano	Spain			
96	Fertiberia Sagunto	Sagunto	Spain			
97	Fertiberia Luchana-B	Luchana-Baracaldo	Spain			
98	Erkimia SA	Tarragona	Spain			
99	Dyno Nitrogen	Ljungaverk	Sweden			
100	Yara	Landskrona (Malmohus)	Sweden			
101	Yara	Koeping (Vastmanland)	Sweden	105000		
102	Yara	Koeping (Vastmanland)	Sweden	136500		
103	Lonza AG	Visp	Switzerland			
104	Du Pont (UK) Ltd	Wilton	United Kingdom			
105	Imperial Chemical Industries ICI	Stevenson (Scotland)	United Kingdom			
106	Grow How UK ltd, Ince (UK)	Ince Marshes (Cheshire)	United Kingdom			
107	Grow How UK ltd (UK)	Ince Marshes (Cheshire)	United Kingdom			
108	RGrowHowal Ordnance Division of Lambson Fine Chemicals	Bridgewater	United Kingdom			
109	Richardsons Fertilizers	Belfast	United Kingdom			

Continuation Table 5

	Company	**Location**	**Country**	**Capacity [t/y]**	**Capacity [t/d]**	**kg N_2O / t 100% HNO_3**
110	Grow How UK ltd Billingham	Billingham	United Kingdom			
111	Grow How UK ltd Billingham	Billingham	United Kingdom			
112	Grow How UK ltd Billingham	Billingham	United Kingdom			
113	Grow How UK ltd Billingham	Billingham	United Kingdom			
114	Grow How UK ltd Severnside	Redwick Severnside (Bristol)	United Kingdom			
115	Grow How UK ltd Severnside	Redwick Severnside (Bristol)	United Kingdom			

Nitric acid production:

Nitric acid is produced in different concentrations:

- weak acid 30-65% (weight) HNO_3
- strong acid 70% or more

The strong acid is produced by concentrating weak nitric acid in downstream extractive distillation units being very energy intensive. The worldwide nitric acid market is represented mainly by weak acid while the strong acid market covers only 10% of the total nitric acid production. However, all strong acid units are downstream the weak acid units so benchmarking weak acid plants will cover all nitric acid plants within the EU ETS.

A high-strength nitric acid (98-99%) can be obtained by concentrating the weak nitric acid in additional extractive distillation units with the help of dehydrating agents (sulphuric acid).

The benchmark study includes both direct emissions and steam export but due to the unavailability of the steam export data for nitric acid production, a benchmark is developed only for the N_2O emissions and steam was not accounted for in the benchmark analysis. The specific emissions are given as N_2O figures. N_2O has a greenhouse gas potential of 310 CO_2-equivalents.

In Europe two types of nitric acid plants are common; single pressure plants and dual pressure plants. If the oxidation and absorption processes happens at the same pressure they are called single pressure plants, if it is different they are called dual pressure plants. Then the absorption process happens at a higher pressure than the oxidation. Based on the 2007-2008 data from AC Fiduciaire for 88 plants their classification and Europe–wide share is as follow:

- Low pressure plants (pressure below 1.7 bar) cover 13% of all nitric acid plants.
- Medium pressure plants (pressure between 1.7 and 6.5 bar) cover 80% of all nitric acid plants.
- High pressure plants (pressure between 6.5 and 13 bar) cover 7% of all nitric acid plants.

It should be noted that the above share is approximate and indicates the pressure of the oxidation process. The most common types of plants are M/H plants (for e.g. 4.5 bar/12 bar). In Europe most of the nitric acid is produced by the high-temperature catalytic oxidation of ammonia, the so called "Ostwald Process". This process typically consists of three steps: ammonia oxidation (a), nitric oxide oxidation (b), and absorption (c), which are described in detail.

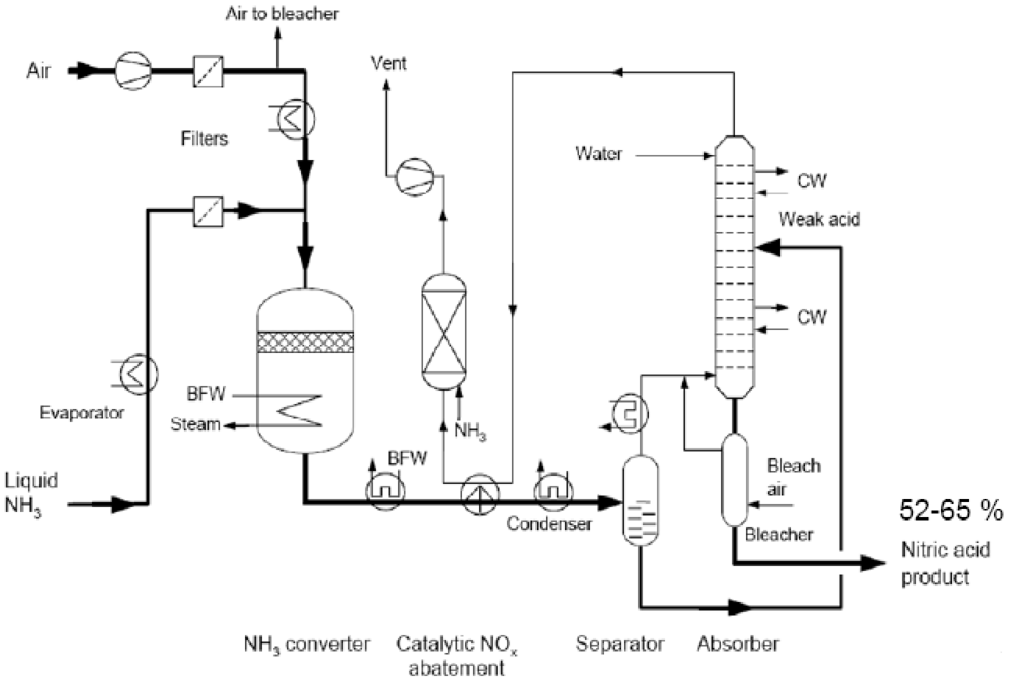


Figure 1 Simplified view of Ostwald-process plant for weak nitric acid production (TU München, 2008)

(a) Ammonia oxidation:

NH_3 is reacted with air on a catalyst in the oxidation section. Nitric oxide and water are formed in this process according to the main equation:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

Equation 1

The most common catalyst is a 90% Palladium / 10% Rhodium gauze constructed from squares of fine wires. Up to 5% palladium is used to reduce costs. A reduction of up to 30% N_2O may be achieved with an improved platinum-based catalyst. The use of two-step catalysts reduces the amount of platinum used by between 40-50% and platinum losses are reduced by 15-30% under similar conditions. Platinum gauzes are used as the first step, and a bed of non-platinum oxide catalyst is used as the second step.

(b) Nitric oxide oxidation:
The nitric oxide is cooled to a temperature of 38 °C at a pressure up to around 7.8 bar. The nitric oxide reacts (non-catalytically) with oxygen to form nitrogen dioxide and dinitrogen tetroxide according to the reaction below

$$4NO + 2O_2 \rightarrow 2NO_2 + N_2O_4$$

Equation 2

The progress of this reaction is highly dependant on the pressure and temperature of the reaction chamber. High pressures and low temperatures favour the production of nitrogen dioxide which is preferred to dinitrogen tetroxide.

(c) Absorption:
After being cooled, both the nitrogen dioxide and the tetroxide mixture enter the absorption chamber. The gaseous mixture is introduced at the bottom of the column while liquid dinitrogen tetroxide and deionised water enter at the top. In this chamber, the absorption takes place on the (bubble cap) trays and oxidation takes place between the trays.

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

Equation 3

Secondary air is fed to the column to further oxidise the NO and to remove the NO_2 from the weak nitric acid. The gas-liquid contacts in the absorption column are designed to increase the oxygen loading in the circulating acid. The produced weak acid leaving the absorption chamber has typically a concentration of 55-65% (weight basis), depending on the temperature, pressure and the number of absorption stages. During the NO_2 absorption, some nitrous acid (HNO_2) formation is possible.

Emissions and by-products:
By-product (tail gas) streams contain NO, NO_2, N_2O, O_2, and H_2O depending on the applied process conditions. The oxidation of ammonia in the reactor generates NO, with N_2O as a by-product. The increase of the combustion pressure from 1 to 5 bar in the last decades has slightly resulted in an increasing of the N_2O emission level. Dual High / High pressure systems show a lower NO yield and generate more N_2O.

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O$$
$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Equation 4

Nitric acid plants have a specific and large variety of different integrated structure and process operation parameters e.g. pressure in the reactor / absorption chamber or type of the catalyst used. Most of the plants are old and have different reactor designs and absorption chamber structures. That is why it is not easy to compare the performance of all the plants and specific abatement techniques cannot be applied homogeneously in all the plants. Below are some of the main technology providers for emission abatement technologies today (as shown in deliveries to worldwide CDM and JI projects):

- High temperature catalytic reduction method (for installation in the high temperature burner reactor): BASF, Heraeus, Johnson Matthew, Umicore, YARA.
- Tail gas catalytic reduction method (for installation in combination with a deNOx unit at high tail gas temperatures): Uhde EnviNox.

Typically the cost of implementing and operating these abatement technologies is commercially priced at 1.5-2 € / t of nitric acid for in-burner techniques, and 5 € / t of nitric acid for tail gas techniques, but this will vary depending on the process design and a wide pressure range from old to new installations and ease of their retrofitting. (EFMA 2009b)

Several emission abatement techniques are commercially available and under further development and testing. They are commonly grouped in three categories, corresponding to three different stages in the nitric acid production process or tail gas treatment:

(1) Primary: Suppression of N_2O formation
This requires modifications to the ammonia oxidation gauzes in order to reduce N_2O formation. According to gauze suppliers, as much as 30-40% reduction of N_2O formation can be achieved in conventional nitric acid plants.

(2) Secondary: Removal of N_2O in the burner after the ammonia oxidation gauzes.
Basically two abatement techniques exist:

(a) *Homogeneous decomposition***:** This implies expanding the volume of the process burner after the ammonia oxidation gauzes to obtain a longer reaction time, thus resulting in homogeneous decomposition of N_2O. This was the design principle of a nitric acid plant built in Norway in 1990/91, which has since operated with approximately 70% reduction in N_2O emissions compared to a conventional medium pressure process design. This is equivalent to 2.5 kg N_2O / t of nitric acid. This technology is in principle only suitable when building new nitric acid plants. Existing nitric acid plants would require extensive and costly rebuilding, if at all possible.

(b) *High temperature catalytic reduction*: This consists of constructing a catalyst basket under the ammonia oxidation gauzes (if not already in place for holding raschig rings supporting the ammonia oxidation metal gauzes), and filling the basket with selective de-N_2O catalyst to promote N_2O decomposition. This has the potential of reducing emissions below 2.5 kg N_2O / t of nitric acid. The level of reduction depends on the design and operating conditions of the nitric acid plant, such as operating temperature and pressure, pressure drop, available space for the basket, the basket size and construction, catalyst performance, and aging characteristics of the catalyst. Several technology suppliers offer this technique for installation in existing plants, e.g. BASF, Heraeus, Johnson Matthew, Umicore, Yara.

(3) Tertiary: Removal of N_2O from the tail gas.
Different catalytic reduction techniques can be applied downstream of the absorption tower in the nitric acid plant:

(a) *Non Selective Catalytic Reduction (NSCR)*: This has been utilised widely in North America and Russia for NOx reductions, and has the 'side-effect' of reducing N_2O emissions. However, the technology has a high energy consumption and results in emissions of other greenhouse gases (CO_2 and CH_4), and of ammonia to air. For these reasons it is not recognized as a sustainable technique for abatement of N_2O emissions by the United Nations JI / CDM project Directives, nor as BAT by the EU IPPC Directive.

(b) *Selective Catalytic Reduction:* This technique reduces the N_2O emissions to a low level, but requires a high tail gas temperature. As such it is only applicable for a certain number of the nitric acid plants in Europe. It is significantly more costly than the in-burner technique. The Uhde EnviNOx process is analogous to this SCR group.

The N_2O emission rate from nitric acid plants without N_2O abatement systems depending on the process is as follow:

- Low pressure plants : 5 kg N_2O / t nitric acid, +/- 10%
- Medium pressure plants (3-7 bar) : 7 kg N_2O / t nitric acid, +/- 20%
- High pressure plants (>8 bar) : 9 kg N_2O / t nitric acid, +/- 40%

An average European plant emits 6 kg N_2O / t 100% HNO_3 corresponding to about 2 t CO_2-equivalents / t 100% HNO_3. N_2O emissions for existing plants are 0.12-1.85 kg N_2O / t HNO_3 100% and for new plants (which are mostly medium / high dual pressure type plants) 0.12-0.6 kg N_2O / t HNO_3 100% (BREF – LVOC, 2007).

3.2 Benchmarking methodology

3.2.1 Background

As already indicated in Section 3.1, the methodology as described here only considers the N_2O emissions from nitric acid production and not the indirect emissions. The production of nitric acid is an exothermic reaction in which steam is generated. According to our approach direct emissions and steam should be accounted for to calculate the emissions. The allocation of allowances to a steam exporting installation is explained in chapter 6.1.5 of the report on the project approach and general issues. This issue is not yet considered in the nitric acid chapter due to the lack of information.

Emissions from nitric acid plants vary substantially depending on different operating pressures, catalysts, concentration of nitric acid and abatement processes. There is no universal abatement technology suitable for all kind of plants.

Although the European plants are within the best plants worldwide, there are many plants without any abatement technology in Europe. Therefore the spread factor of specific N_2O emissions is very high in this sub-sector. Nevertheless one emission benchmark can be developed for all plants.

The consortium proposes to exclude plants with NSCR abatement technique from benchmarking for two reasons[2]:

NSCR is not approved in the reference documents (BREF) as Best Available Technology (BAT), above all because of the higher energy consumption (which might be taken into account if also steam emissions would be accounted for in the benchmark) and ammonia emissions. Normally this argument is not conclusive to justify an exclusion of NSCR plants since there are a lot of plants in other sectors being not BAT but included in the benchmarking. However, non-BAT plants are usually positioned at the right hand side of the benchmark curve. In the case of NSCR, an explicit abatement technology, those plants are positioned at the left hand side, since the NSCR technique lowers the GHG emissions significantly (but with other, negative environmental effects, see above)[3]. By including them in the benchmark curve, the benchmark value would be dominated (or at least influenced) by a technology that operators are not allowed to install because of not being BAT. A full environmental life cycle assessment would be necessary if the use of NSCR technology has an overall net positive environmental effect.

But also just focusing on the GHG emissions is problematic. The use of the NSCR technique releases methane (CH_4) emissions. Methane is not mentioned in the amended Directive as greenhouse gas to be monitored, so there is no legal obligation to measure it. And without including CH_4 besides N_2O and CO_2, the overall GHG intensity of NSCR plants is not reflected in the benchmarking.

The consortium proposes not to exclude plants with Uhde EnviNOx abatement technique from benchmarking as is suggested by EFMA. After extensive discussions with the technology provider, we found that it is possible to adopt EnviNOx also to those plants having a low tail gas temperature (approx. below 330 °C) by heating of the tail gas and heat recuperation by using energy from the exothermic N_2O decomposition and in plants equipped with in-burner catalyst techniques as second step.

An exclusion of the Uhde EnviNOx technology from benchmarking would ignore the spirit of the amended Directive, to foster GHG reduction measures. If the EnviNOx plants are left outside the benchmarking they will be treated in a fallback approach, while they would be rewarded by getting additional free allowances if they were included and within the best 10% performers. For other companies there would be no incentive to use this technology and companies that already have invested in this technology would not benefit.

---

[2] This is also the opinion of EFMA (European Fertilizer Manufacturers Association).

[3] Plants with NSCR abatement have a maximum emission intensity of 1.3 kg N_2O/ t nitric acid (average: 1.0 kg N_2O/ t nitric acid). Including those plants would position them below the benchmark level on the left hand side of the curve and lower the overall benchmark level.

Finally it should be remarked that the Uhde EnviNOx technique has been acknowledged as BAT for official approval procedures in the European Union. Uhde EnviNOx is a proven technology and already in advanced application on a commercial scale, e.g. since 2000 at AMI Linz. Furthermore an Abu Qir Fertilize plant in Egypt, being one of the world's largest fertilizer producers, is equipped with this technique as well and it has been approved as first CDM methodology for N_2O emission reduction in nitric acid plants.

3.2.2 Final proposal for products to be distinguished

The production of nitric acid belongs to NACE code 20.15 and the PRODCOM number is 20.15.10.50. The reference product is 1 t of 100% nitric acid and since the methodology focuses on N_2O emissions only, no further differentiation is required between weak and strong acid plants.[4]

3.3 Benchmark values

3.3.1 Background and source of data

Nitric acid producers are represented by EFMA whereas the benchmarking study ordered by EFMA for nitric acid plants is carried out by the independent auditor company AC-Fiduciaire. A benchmarking study based on 2007/08 for 90 nitric acid plants out of the 115 EU-27 plants is available. Missing plants do not belong to the. The results of this benchmark study have been provided to the consortium.

---

[4] If steam would be included in the curves, a further decision is required on whether separate benchmarks for weak and strong acid would be required.

3.3.2 Final proposed benchmark values

The following three figures show the outcome of the 2007/2008 benchmark study:

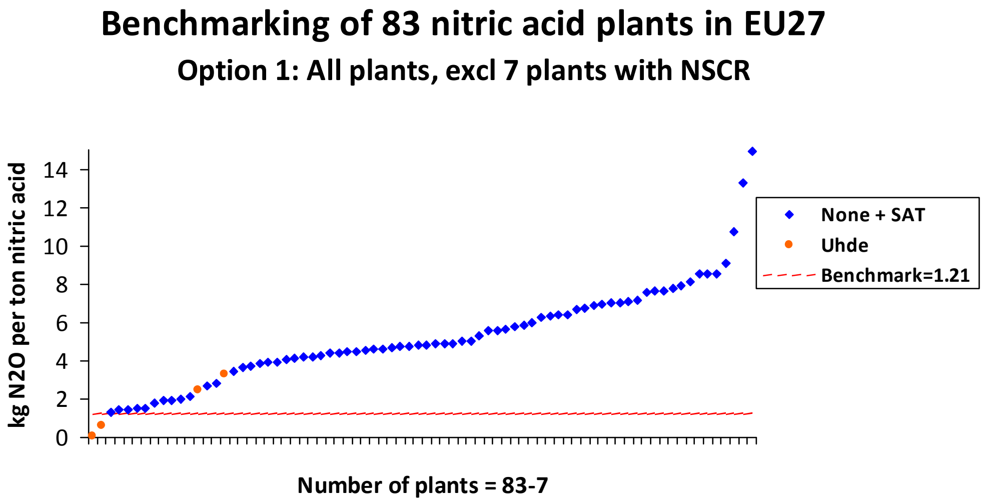


Figure 2 N_2O emissions from EFMA nitric acid plants 2007-08, excluding plants with NSCR abatement technique (EFMA 2009a)

The benchmark curve in Figure 2 includes all plants except for the plants with NSCR abatement technique. According to EFMA the benchmark level for this curve is **1.21 kg N_2O / t HNO_3**. This value is below the value of 1.3 kg N_2O / t HNO_3 that is the benchmark in 2012 for existing nitric acid installations that are unilaterally included by the Netherlands in the second trading phase of the EU ETS (EC, 2008).

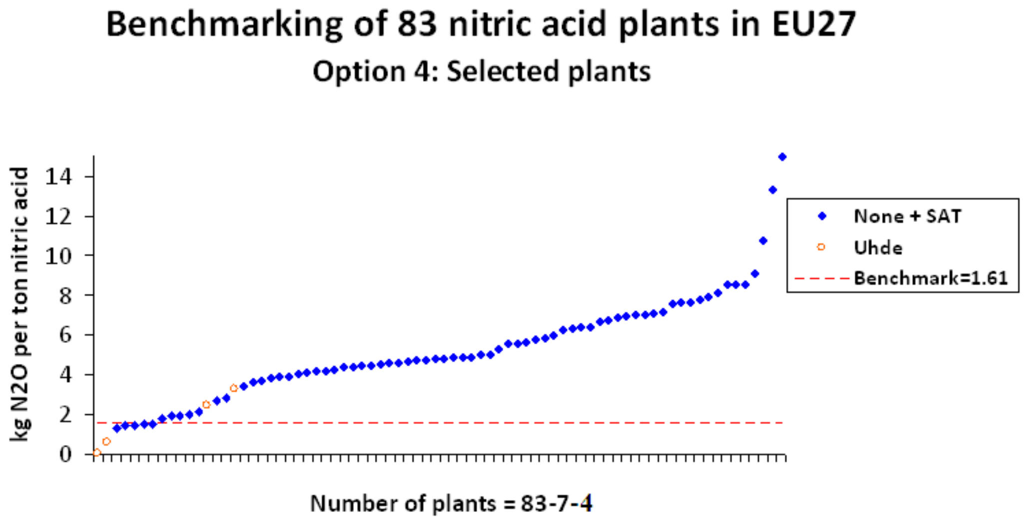


Figure 3 N_2O emissions from EFMA nitric acid plants 2007-08, excluding plants with Uhde EnviNOx and NSCR abatement technique (EFMA 2009a)

The second benchmark curve in Figure 3 excludes besides the plants with NSCR abatement technique also the plants with Uhde abatement technique. **However, the consortium arrives at the decision, that the exclusion of plants with Uhde EnviNOx abatement technique is not justified.** According to EFMA the benchmark level for this benchmark curve is 1.61 kg N_2O / t HNO_3.

3.3.3 Possibility of other approaches

There are no reasons for other approaches.

3.4 Stakeholder comments

In discussion on September, 2009, EFMA comments against the NSCR abatement technology are as below:

Only a very few nitric acid plants in Europe operate with NSCR units, developed many years ago to reduce NOx emissions. The technology has a positive side effect in reducing N_2O emissions to a very low level. However, NSCR requires considerable energy consumption and leads to significant methane emissions in addition to CO_2 and ammonia to air. For this reason, NSCR is not approved as best available technique in the reference document on best available techniques for the fertilizer industry (BREF – LVOC, 2007). In effect, the industry is not allowed to install such technology in any new or existing plant in Europe.

Though NSCR techniques promises comparatively much lower N_2O emission level, it is not clear how much they are reducing GHG emission because of methane slippages and other secondary emissions. As an example of the emissions from an NSCR unit, the following are typical average values (EFMA 2009b):

N_2O = 50 ppm = 0.3 kg N_2O / t nitric acid
CH_4 = 4500 ppm = 10 kg CH_4 / t nitric acid = 0.6 kg N_2O-eq / t nitric acid
CO_2 = 1000 ppm = 6 kg CO_2 / t nitric acid = 0.02 kg N_2O-eq / t nitric acid
NOx = 150 ppm
NH_3 = 100 ppm

These emissions apart from NOx are normally not monitored. For some plants the methane slip can be as high as 7000 ppm, resulting in an overall N_2O-eq emission of approx 1.3 kg N_2O / t nitric acid. Only 7 of the 88 plants in the AC Fiduciaires study 2007-2008 are fitted with NSCR.

The N_2O emission from the nitric acid plants with NSCR only represents 0.2% of the total N_2O emission from all nitric acid plants in Europe. The emission level is in the range 0.1-0.3 kg N_2O / t of nitric acid. Accounting for the addition of the methane and CO_2 emission related to the high energy consumption, the N_2O-equivalence is raised to the range of 0.6-1 kg N_2O / t of nitric acid. These emissions, however, are not regularly monitored in the plants.

EFMA strongly claims that nitric acid plants with NSCR should be excluded from the benchmarking calculations, since the industry are not allowed to take this technology into use, and since NSCR leads to additional energy consumption and ammonia emissions to air. The benchmarking must be based on techniques that can be applied!

To avoid windfall profits for nitric acid plants that are currently operating with NSCR, a fixed level of N_2O-eqv from such plants can be agreed.

EFMA comments against the Unde ENviNOX abatement technology are as below:
One technology supplier (Uhde) offers today a solution for reduction of N_2O emissions down to below 0.3 kg N_2O / t of nitric acid. This is a significant achievement, but can only be applied to a small number of nitric acid plants since it requires a high tail gas temperature. Most of the plants in Europe have already invested in different N_2O reduction techniques, in line with what is occurring on the global arena in CDM and JI projects. Less than 10% of the plants in Europe have a realistic opportunity for installing the Uhde technology. EFMA finds it unjustified that this technology should be part of setting the benchmark level in Europe, because this will create a monopoly supplier situation. For the benchmarking methodology in general, the Commission has emphasised that they will not differentiate between process technologies and energy sources. Hence, the Commission should not adopt a different principle when it comes to setting the benchmark level for nitric acid plants, i.e. the benchmark level should not be ruled by one technology from a single supplier.

Applicability of lower temperature Uhde Technology
The tertiary abatement technology from Uhde that is well tested en proven operates at high temperatures only and is only practical for use at tail gas temperatures above 400 degrees Celsius. Of the 83 Nitric acid plants in the EFMA survey 17 plants have tail gas temperatures above 400 degrees Celsius, 4 plants already apply Uhde technology and 18 plants have chosen for secondary abatement, which leaves only 6 plants which are undecided. In other words, the Uhde technique will not be applied for 90% of the plants (60% cannot utilize this technique, and 30% operate alternative abatement techniques).
There is lower temperature technology available which is proven in a few installations outside Europe. This technology requires the addition of Natural gas or Propane as additional feedstock for the abatement. The Natural Gas does provide methane slip which results in additional methane emissions and also Carbon monoxide and Carbon dioxide emissions which counteract the N_2O Green house gas reduction effect. Outside Europe this effect is less important since CDM projects credit the whole abatement from the inlet of the reactor, therefore this technology is found in a few CDM projects outside Europe. Economically the operational cost of the additional Natural Gas and the additional CO_2 emissions reduces the economic feasibility versus a secondary catalyst to a great extend. It is therefore the opinion of the Nitric acid producers that Uhde technology in Europe is only technically and economically competitive for large Nitric acid plants (> 400000 metric t / year) with tail gas temperatures above 450 degrees Celsius. Within EFMA there is only one plant (1%) that fits within this category that did not apply a N_2O abatement technology

The benchmark established for opt-in 2012 is 1.3 kg N_2O / t of nitric acid. This is a strict level when considering that a number of European nitric acid plants cannot fully utilise the new abatement technologies, because of processing and design constraints. The N_2O benchmark level should be lifted to at least 1.5 kg N_2O / t of acid, which is the opt-in level for 2010-11.

Heat generated from exothermic process of nitric acid production
EFMA claims that the nitric acid plants shall obtain a credit for the heat generated by the exothermic process of the nitric acid production, if utilised for steam production or for heating. This heat generation is not associated with any CO_2 emission. It replaces the need for using fossil fuels thus saving CO_2 emissions.

The European fertilizer industry is seriously concerned about the EU benchmarking approach for establishing emission allowances from 2013. The fertilizer industry is judged by the Commission to be the most exposed sector for carbon leakage.

3.5 Additional steps required

EFMA was reluctant to include the plants with NSCR abatement technique. In order to judge the influence of the NSCR plants on the benchmark level, it is absolutely necessary to have a curve available including those plants.

Furthermore, ideally also the steam export from nitric acid plants should be taken into account and based on this assessment, a decision is required on whether a differentiation between weak and strong nitric acid would be required.

Finally it has to be discussed how emission data from non-EFMA members could be made available and how they influence the final benchmark value.

4 Steam cracking

4.1 Production process

The European steam crackers account for about 18% of the total GHG emissions from the chemical industry in the EU. The following table lists all steam crackers in the EU as well as their location, operator and ethylene capacity.

Table 6 Steam crackers in the EU (APPE 2009a)

Country	Location	Company	(Ethylene) Capacity [kt/y]
Austria	Schwechat	OMV	500
Belgium	Antwerp	FAO	255
	Antwerp	FAO	550
	Antwerp	FAO	605
	Antwerp	BASF	800
Bulgaria	Burgas	Neftochim	300
	Burgas	Neftochim	150
Czech Republic	Litvinov	Chemopetrol	485
Finland	Kulloo	Borealis	330
France	Berre	Basell	470
	Carling	ATOFINA	570
	Dunkerque	Copenor	380
	Feyzin	A.P. Feyzin	250
	Gonfreville	ATOFINA	525
	Lacq	ATOFINA	75
	Lavera	Naphtachimie	740
	ND	ExxonMobil	425
Germany	Böhlen	BSL	565
	Burghausen	OMV	345
	Gelsenkirchen	BP	450
	Gelsenkirchen	BP	525
	Heide	RWE-Shell & DEA Oil	100
	Köln-Worringen	BP Köln	1100
	Ludwigshafen	BASF	220
	Ludwigshafen	BASF	400
	Munchmunster	Veba Oil	320
	Wesseling	Basell	1043
	Wesseling	RWE-Shell & DEA Oil	520
Greece	Thessaloniki	EKA	20
Hungary	Tiszaujvaros	TVK	360
	Tiszaujvaros	TVK	250
Italy	Brindisi	Polimeri Europa	440
	Gela	EniChem	245
	Priolo	EniChem	745
	Porto Torres	EniChem	250
	Porto Marghera	EniChem	490
Netherlands	Geleen	Sabic Europe	590
	Geleen	Sabic Europe	660
	Moerdijk	Shell	900
	Terneuzen	Dow	580
	Terneuzen	Dow	590

Continuation Table 6

Country	Location	Company	(Ethylene) Capacity [kt/y]
	Terneuzen	Dow	650
Poland	Plock	Polski Koncern Naftowy ORLEN	360
Portugal	Sines	Borealis	370
Romania	Pitesti	Arpechim	200
Slovakia	Bratislava	Slovnaft	200
Spain	Puertollano	Repsol	250
	Tarragona	Repsol	650
	Tarragona	Dow	600
Sweden	Stenungsund	Borealis	620
UK	Fawley	ExxonMobil	126
	Grangemouth	BP Amoco	1020
	Mossmoran	ExxonMobil / Shell	830
	Wilton	Huntsman	865

Steam cracking is the worldwide most important process to produce basic chemicals by cracking long-chain hydrocarbons into short-chain hydrocarbons. The most important products are ethylene, propylene, butadiene (representative for the C4 fraction, benzene (representative for the aromatics) and hydrogen (representative for the crack gas). Those products can be summarized by the term high value chemicals (HVC). Ethylene is the petrochemical with highest production volume in the EU and the Basic chemical for about 30% of all petrochemicals. The ethylene and butadiene demand is covered completely by steam cracking. The demand of benzene is partly covered by the steam cracking (2/3) and reforming (1/3) process. Most of the propylene is produced with steam cracking. The rest is produced in refineries in the catalytic cracking section, by dehydrogenation of propane and metathesis. Metathesis can be applied to convert ethylene and C4 hydrocarbons to propylene as a stand alone process or being integrated into a steam cracker perimeter.

The steam cracking process can be operated with different feedstocks. In Europe Naphtha is the most used feedstock (73%), followed by gas oil (10%) and gaseous feedstocks (17%) like LPG (butane, propane) and ethane.

The feedstock influences the product mix as well as the specific energy consumption and the specific CO_2 emissions. The lighter the feedstock, the higher the share of ethylene in the product mix. With increasing share of carbon molecules in the feedstock, the share of further by-products increases. Generally spoken, the emissions per t of ethylene are lower using light feedstocks and higher using heavy feedstocks. However, per t of HVC both light and heavy feedstock show higher specific emissions compared to naphtha and the differences in specific emissions due to different feedstocks are smaller expressed per t of HVC as compared to ethylene.

Steam cracking is endothermic, since for cracking hydrocarbons a lot of energy is necessary. The feedstock is mixed with steam and piped through the tubes of the crack furnace (700°C-900°C). The tubes are heated by combusting fuel in external burners. In this way combustion-related CO_2 emissions are released.

4.2 Benchmarking methodology

4.2.1 Background

The consortium proposes to relate the emission benchmarks to the HVC's. This approach has two advantages:

- As a principle benchmarks have to be developed for every marketable product. Since 5 marketable products (ethylene, propylene, butadiene, benzene and hydrogen) are produced at the same time, 5 benchmarks would have to be developed, if the benchmarks are related to a single product, but it would be impossible to allocate the emissions to each of the products produced. Relating the benchmarks to the total marketable product mix (HVC) reduces the number of benchmarks and results in one overall metric for the steam cracking process eliminating the need to allocate emissions to the individual products. All products would be included within one benchmark.
- The feedstock influences the product mix and the specific emissions. Basing the benchmarks on the HVC's allows for this fact and the influence on the specific emissions would be minimal.

According to our principle "one product, one benchmark" no differentiation should be made between different feedstocks, fuels or techniques (see chapter 4.4.2 in the report on the project approach and general issues). That is why no feedstock correction factor should be included in the allocation formula.

There are some crackers being operated in parallel lines. There is the possibility to crack the feedstock in line one and to separate the cracked gas in line two (see Figure 4). As a consequence most of the emissions emerge in the line one cracker whereas the product is leaving line two. Without accounting this would result in high specific emissions in line one and low specific emissions in line two. The line one cracker would be positioned at the right hand side in the benchmark curve and the line two cracker at the left hand side, what does not necessarily reflect the actual emission efficiency of the crackers. Furthermore it is possible to feed a line with supplementary feed which has been either cracked in the past and stored temporarily or has been delivered from an external utilisation (see Figure 4). Supplementary feed which is already cracked does not generate a lot of emissions but increases the production of HVC and therefore decreases the specific emissions.

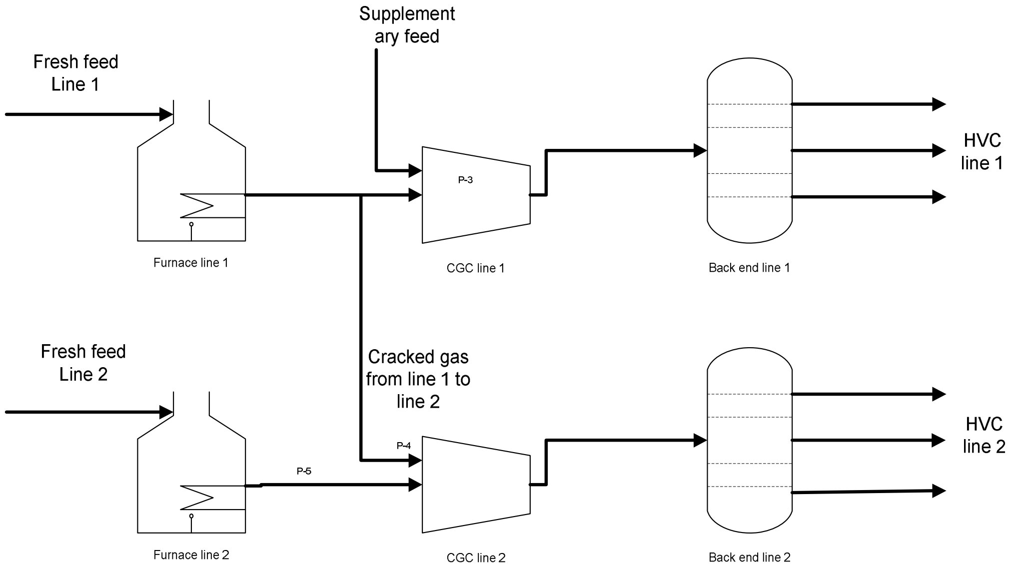


Figure 4 Cracker configuration with supplementary feedstock and different cracking and separation lines (APPE 2009c)

That is why the consortium agrees with APPE to include a supplementary feed factor which accounts for different lines and supplementary feed. The idea is to assign the emissions to that cracker, where the HVC has passed the furnace, considering corrections for the emissions related to the energy consumption of the back end. The calculation of the specific emissions is illustrated by the following simplified equation:

$$Specific\ CO2\ emissions = \frac{Direct + steam\ CO2\ emissions - corr\ HVC_{sup\ feed} + corr\ HVC_{to\ line2}}{(total\ HVC_{ex\ backend} - HVC_{sup\ feed} + HVC_{to\ line\ 2})}$$

Equation 5

The direct and steam emissions are the actual emissions emerging from the furnace and the back end of the line 1 cracker in Figure 4. Emissions being released at the back end, related to the supplementary feedstock, are deducted from those emissions and the released emissions in the back end of the line 2 cracker, related to the HVC being switched from line 1 to line 2, are added to the emissions of the line one cracker. The same corrections have to be made for the HVC flow. In this way only those emissions are assigned to the line 1 cracker, which indeed result from the HVC having passed the furnace of this cracker. The emissions being released by the supplementary feed are assigned to the cracker where the HVC have been cracked.

Finally, there are electro-intensive crackers being within the best 10 percent of all European crackers when considering only direct emissions and emissions from the production of steam, whereas these crackers are not within the best 10 percent when considering additionally the emissions from the production of electricity. Electro-intensive crackers may export steam which is compensated by a higher consumption of electricity. As a result, when only considering direct emissions and emissions from the production of steam the average best 10 percent benchmark value does not necessarily reflect the emissions of the most energy efficient installations and therefore influences the benchmark value in a negative way for the competitors.

We propose to decide whether to account for the interchangeability of steam and electricity as energy carriers not until we know to what extent the final benchmark value is influenced by the electro-intensive crackers. In exceptional cases (if there is a wider influence) the interchangeability could be accounted for as described in chapter 6.3 in the report on the project approach and general issues. Thus the determination of the average best 10% benchmark value takes into account the emissions from the combustion of fuel, the production of steam and electricity (calculated by means of a uniform emission factor for electricity). However, free allowances may only be given for direct emissions (fuel and steam), even if the benchmark value allowed for more free allowance since no free allowances should be given for electricity production.

In the cracker furnaces, the waste gas (containing significant amounts of methane) produced within the cracker is often used, supplemented by other fuels. It could therefore be considered to apply in the calculation of the emission intensity for steam crackers the method considering waste gas (see Section 6.2 of the report on the project approach and general issues) to bring different configurations that either use the gas in the cracker or in other units on the site at an equal footing. This needs further discussion once the benchmark curve for 2007 / 2008 is available.

4.2.2 Final proposal for products to be distinguished

The steam crack process belongs to NACE code 20.14 and the PRODCOM numbers of the marketable products (HVC's) are the following:

- Ethylene: 20.14.11.30
- Propylene: 20.14.11.40
- Butadiene (C4 fraction): 20.14.11.65 (for butadiene), for the C4 fraction there is not an own PRODCOM number, it falls in 20.14.11.(50-90) (acyclic hydrocarbons)
- Benzene (Aromatics): 20.14.12.23 (for benzene), the aromatics fall in number 20.14.12 (cyclic hydrocarbons)
- Hydrogen (Crack gas): 20.11.11.50 (for hydrogen), other crack gases fall in 20.14.11.20 (saturated acyclic hydrocarbons)

The benchmark covers the end products ethylene and propylene as well as the C4 fraction, the aromatics and the crack gas. The latter are product mixtures with butadiene, benzene and hydrogen as their representatives. The reason why partly end products and partly product mixtures are covered is due to the included and excluded (downstream) units:

The following units are included in the benchmarking:

- Acetylene hydrogenation
- Ethylene splitter
- Propylene splitter

Excluded from benchmarking are:

- Hydrogen (pressure swing adsorption)
- C4 extraction
- Aromatics extraction
- Hydrotreating of pyrolysis gas

The upper units are excluded because not every steam cracker is equipped with them. As a result they cannot be included in the steam cracking process and emissions related to these process steps should be dealt with via the fall-back approach (see section 5 of the report on the project approach and general issues).

4.3 Benchmark values

4.3.1 Background and source of data

The petrochemical industry is represented by APPE (Association of Petrochemical Producers in Europe). APPE founded the Energy Study Team, a task force representing more than 90% of the European production capacity. The group was created in summer 2007 to follow the ETS developments and to initiate a CO_2 benchmark for petrochemicals. Two subgroups have investigated on the one hand the perimeter of installations and processes, and on the other hand the methodology (direct emissions – energy uses – production figures). 12 major petrochemical operators provided financial resources for the process.

APPE assigned Solomon Inc. to collect emission data of all steam crackers in the EU. Today an emission benchmark curve is available for the years 2005-2007 including 47 out of 55 steam crackers in the EU. A revised questionnaire for the 2007-2008 data has been prepared and the survey has been completed. The actual data are now in the hands of Solomon for verification. Up to now the benchmark curve based on those 2007-2008 data is not yet available.

4.3.2 Final proposed benchmark values

According to the reference document on BAT (BREF – LVOC, 2003) emission factors < 700 kg CO_2 / t HVC can be achieved by steam crackers. The same value is given by APPE as indicative reference value (APPE 2009b).

The following Figure 5 shows the indicative benchmark curve from the 2005-2007 benchmarking carried out by Solomon. Steam is included by using an emission factor of 0.0622 t CO_2 / GJ heat which underlies an efficiency of 90%, natural gas as feedstock and condensate returns of 60 °C. According to APPE there will be many differences between the 2005-2007 curve and the upcoming 2007-2008 curve. The old curve does not account for plant specific steam factors as well as for corrections for supplemental feed and the interchangeability of steam and electricity, which will have a significant effect on the shape of the curve and the benchmark value. That is why the old curve is shown without absolute figures at the ordinate. The figure 100 roughly corresponds to the average best 10% of all plants. The proportions are identical compared to the absolute figures.

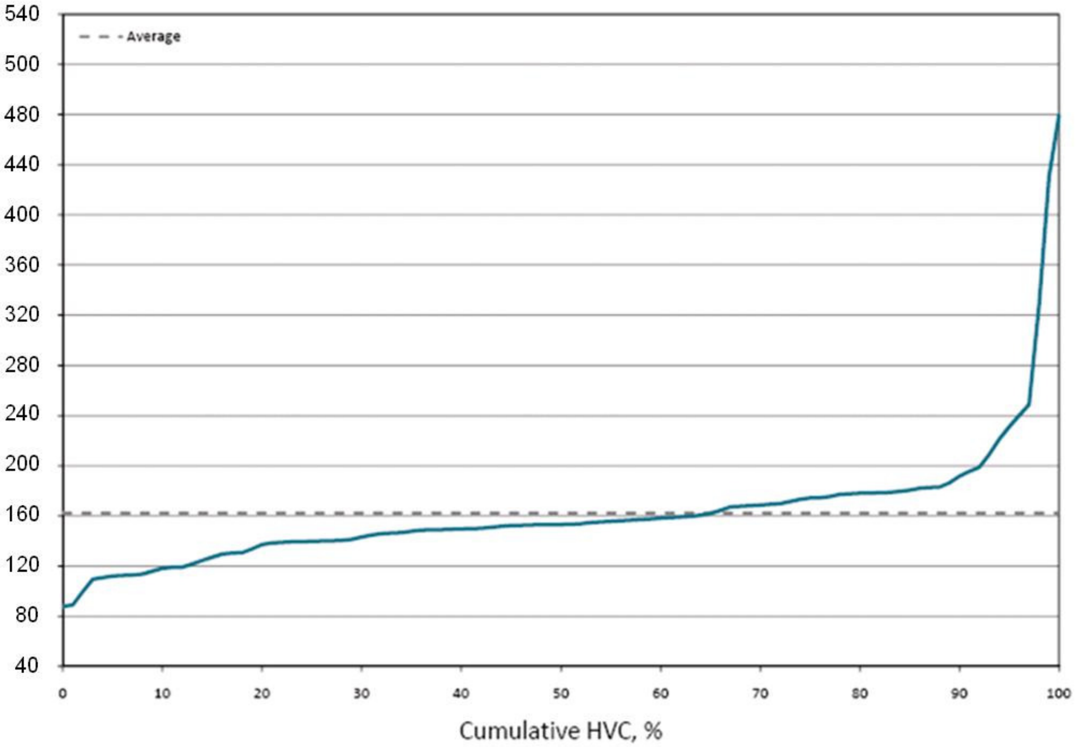


Figure 5 Tentative emission benchmark curve by Solomon without absolute figures; data based on the years 2005-2007; coverage: 47 out of 55 plants (APPE 2009d)

The curve has been smoothed both on the left hand and on the right hand side and the abscissa shows the cumulative production of HVC instead of the individual plants. Deriving a benchmark value from this curve would result in a weighted average benchmark which is in contradiction to the provisions of the EU ETS.

However, APPE provided average data for the best 4 plants (corresponding to the average best 10%), the quartiles, the worst 4 plants and the total average (dashed line). The first quartile (11 plants) is by 18% more emission intensive than the average best 10%, the second quartile (12 plants) by 46%, the third quartile (10 plants) by 62%, the fourth quartile (14 plants) by 137% more emission intensive. The worst 4 plants are by 261% more emission intensive than the average best 10%, whereas the average of all plants is by 70% more emission intensive.

Since the evaluation of the latest benchmark study is under way, it is anticipated that the final proposed benchmark value will be determined at the latest by end of April 2010.

The final benchmark value will differ from the one resulting from the 2005-2007 benchmark study. That is why only a benchmark spread is given at this point: the final benchmark value is between 500 and 700 kg CO_2 / t HVC.

4.3.3 Possibility of other approaches

There is no reason for other approaches.

4.4 Stakeholder comments

APPE petrochemicals are defined by the production of all products of steamcracker / PDH / Metathesis units and the associated chemicals as well as polymers which use a significant amount (on a mole basis) of one or more of the steamcracker / PHD / Metathesis products. Currently 25 products have been identified under APPE petrochemicals (see chapter 1)

There should be a joint equal treatment between products in the chemical (Cefic) and refinery sector (Europia):

- Aromatics
- C3 splitters
- Cumene
- Cyclohexane

Production data should be based on the time period 2004 to 2008, what corresponds to a cracker cycle (+/- 1 year).

The allocation formula must account for the planned, initiated and or partial execution of production extensions in the period 2009 to mid 2011

There should be access to the new entrants reserve for capacity expansion growth and debottlenecking after mid 2011

The allocation formula should account for supplementary feed, different feedstocks and the interchangeability of steam and electricity.

Up to now it has been demonstrated that supplemental feeds, feedstock type and interchangeability of energy carriers have an impact on the representativeness of the top 10% performance. Many other factors could have an impact such that the representativeness of the top 10% performance could always raise questions. It is strongly advised to apply the linear extrapolation algorithm to assure that non-representativeness of the top 10% is avoided by the use of the proposed statistical correction method.

4.5 Additional steps required

It is necessary to derive the benchmark level from a benchmark curve based on 2007-2008 data. This further work should investigate the use of supplementary feed and electro-intensive crackers and should have the individual plants on the x-axis of the benchmark curve. Furthermore it should be further discussed how the use of waste gas by steam cracking units is accounted for in the Solomon methodology.

5 Ammonia

5.1 Production process

Ammonia is produced by the Haber-Bosch process. In this process, nitrogen and hydrogen are converted according to the following chemical equation:

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta H_0 = -91{,}6\,kJ\,/\,mol$$

Equation 6

The ammonia synthesis is exothermic and no greenhouse gases are directly emitted by this process step. However, the production of hydrogen is very energy- and emission-intensive and cannot be considered as a separate upstream process step since ammonia plants are highly energy and material integrated. The production of synthesis gas which intervenes in the production of hydrogen , the incorporation of air (nitrogen), the CO shift conversion to CO_2 and its capture as well as the ammonia synthesis itself are carried out in one single plant. In Europe there are two different processes to produce hydrogen (synthesis gas):

- Steam reforming
- Partial oxidation

In the following those two processes are shortly explained:

<u>Steam reforming</u>:

In the EU more than 90% of the hydrogen for ammonia production is made by steam reforming with natural gas as feedstock. In a first step natural gas and water (steam) are converted to CO and H_2 (synthesis gas). In order to produce more hydrogen from this mixture, more steam is added and the water gas shift reaction is carried out. In this shift conversion step the whole generated CO is converted to CO_2. Those process-related CO_2 emissions emerge from the chemical feedstock conversion.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_0 = 206\ kJ\,/\,mol$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_0 = -41\,kJ\,/\,mol$$

Equation 7

This conversion takes part in the primary and secondary steam reformer at high process temperatures (700°C-1000°C). The necessary heat for the endothermic reaction is generated by combustion of a part of the feedstock. This results in combustion CO_2 emissions.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Equation 8

Partial oxidation:

The remaining hydrogen for ammonia production is produced with partial oxidation. The feedstock for this process is heavy hydrocarbons such as vacuum residues (heavy fuel oil) or coal. Today there are three plants which are fed with heavy hydrocarbons. Two are based on heavy fuel oil (Brunsbüttel, Germany; Amoniaco de Portugal, Portugal) and one on LPG. There is no ammonia plant based on coal in Europe today. However, Poland intends to develop their coal reserves to reduce the dependency on Russian natural gas.

The feedstock is - as the name implies - partially oxidised. This means that the amount of oxygen does not suffice to convert the feedstock completely. Since the share of hydrogen in coal is nearly zero, steam is added in the process. In the following shift conversion step the whole generated CO is converted to CO_2. The process can be described by the following equations:

$$\text{Feedstock vacuum residues: } C_nH_m + \frac{n}{2}O_2 \rightarrow nCO + \left(\frac{m}{2}\right)H_2 \text{ with } n \geq m$$

$$\text{Feedstock coal: } C + H_2O \rightarrow CO + H_2 \text{ and } C + \frac{1}{2}O_2 \rightarrow CO$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_0 = -41\,kJ/mol$$

Equation 9

The partial oxidation of the feedstock is exothermic, so there is no need to combust fuel additionally and all produced CO_2 emissions are to be considered as process-related emissions.

The main component of natural gas is methane. The equation, describing the steam reforming process, shows a H_2:CO ratio of 3:1. In the equation, describing the partial oxidation of heavy hydrocarbons, in particular acetylene (C_2H_2) which is one of the lightest components of vacuum residues, the H_2:CO ratio is 1:2. Partial oxidation of coal results in a H_2:CO ratio of 1:1. Since H_2 is the educt for the ammonia synthesis and all CO is converted to CO_2, the CO_2 emissions emerging from the partial oxidation process are always higher than those from steam reforming. The same is valid for the energy consumption. The feedstock / H_2 ratio is 1:3 for steam reforming and at least 1:1 for partial oxidation. The reason for this is on the one hand the different feedstock use (light / heavy) and on the other hand the different conversion of the feedstock (reaction with water / oxygen). The higher share of carbon in heavy feedstocks compared to lighter feedstock results in higher CO_2 emissions.

As mentioned in previous parts of this chapter the generated CO_2 is captured from the process gas. Some ammonia plants are operated with downstream utilities which use the captured CO_2 as feedstock:

$$2NH_3 + CO_2 \rightarrow [H_2N - CO = O]NH_4$$
$$[H_2N - CO = O]NH_4 \rightarrow (H_2N)_2 - C = O + H_2O$$

Equation 10

The total CO_2 emissions from ammonia plants with downstream urea plants are therefore lower than those without urea plants.

For commercial use there is only one purity grade of ammonia leaving the plants and due to the fact that the production of hydrogen as well as the ammonia synthesis takes part in a highly integrated process, no intermediate products are marketable and ammonia is the only main product. If one follows the principle of developing product specific benchmarks rather than process specific benchmarks and that the benchmarks should not distinguish between different feedstock / fuels, the two different processes, which lead to exactly the same product, should not be considered separately, but as two processes to produce one product. As a consequence there is only one benchmark to be developed for the production of ammonia.

5.2 Benchmarking methodology

5.2.1 Background

The European ammonia production accounts for about 16% of the total GHG emissions from the chemical industry in the EU. The following table lists all ammonia plants in the EU as well as their locations, operators and capacities.

Table 7 Ammonia plants in the EU (BREF – Ammonia, 2007a; EFMA 2009d)

No	Country	Location	Operator	Plant	Capacity [t/d]
1	Austria	Linz	AMI Agrolinz Melamine International GmbH	Agrolinz 1	1520
2	Austria	Linz	AMI Agrolinz Melamine International GmbH	Agrolinz 2	
3	Belgium	Antwerpen	BASF Antwerpen NV	BASANT	1800
4	Belgium	Tertre	Kemira GrowHow SA	Kemira Tertre	1200
5	Bulgaria	Varna, Devnia	Agropolychim,		?
6	Bulgaria	Vratza	Chimco AD		1350
7	Bulgaria	Dimitrovgrad	Neochim		1150
8	Czech Rep.	Litvinov	Chemopetrol		1150
9	Estonia	Kothla-Jarve	Nitrofert		500
10	France	Grand Quevilly	Grande Paroisse SA	GP AM2 Rouen	1150
11	France	Grandpuits	Grande Paroisse SA	GP Grandpuits	1150
12	France	Ottmarsheim	PEC RHIN	PEC-Rhin	650
13	France	Le Havre	YARA	Yara Le Havre	1000
14	France	Pardies	YARA Pardies	Yara Pardies	450
15	Germany	Ludwigshafen	BASF AG	BASF Ammoniakfabrik 4	2400
16	Germany	Piesteritz	SKW Piesteritz GmbH	SKW 1	3300
17	Germany	Piesteritz	SKW Piesteritz GmbH	SKW 2	
18	Germany	Brunsbüttel	YARA Brunsbüttel	Yara Brunsbüttel	2000
19	Germany	Domagen	INEOS Köln GmbH (IVA)		900
20	Germany	Gelsenkirchen	Ruhr Oel (non IVA)		1250
21	Greece	Nea Karvali	Phosphoric Fertilizer Ind.		400

Continuation Table 7

No	Country	Location	Operator	Plant	Capacity [t/d]
22	Hungary	Pétfürdo	Nitrogénművek Rt.	Nitrogénművek NH3	1070
23	Italy	Terni	Yara - Nuova Terni Ind. Chimiche	Yara Terni	?
24	Italy	Ferrara	Yara Italia S.p.A.	Yara Ferrara	1500
25	Latvia	Krievu sala	Gazprom		?
26	Lithuania	Jonavos raj.	SC ACHEMA	Achema Ammonia 1	3000
27	Netherlands	Geleen	DSM Agro B.V.	DSM AFA-2	2700
28	Netherlands	Geleen	DSM Agro B.V.	DSM AFA-3	
29	Netherlands	Sluiskil	Yara Sluiskil	Yara Sluiskil	900
30	Netherlands	Sluiskil	Yara Sluiskil	Yara Sluiskil	1500
31	Netherlands	Sluiskil	Yara Sluiskil	Yara Sluiskil	1750
32	Poland	Wloclawek	Anwil SA	Anwil Ammonia A	750
33	Poland	Wloclawek	Anwil SA	Anwil Ammonia B	
34	Poland	Police	Zaklady Chemiczne POLICE SA	Zaklady Police A	1500
35	Poland	Police	Zaklady Chemiczne POLICE SA	Zaklady Police B	
36	Poland	Kedzierzyn	Zaklady Azotowe		500
37	Poland	Pulawy	Zaklady Azotowe		2680
38	Poland	Tarnow	Zaklady Azotowe		530
39	Portugal	Lavradio	AP-Amoníaco de Portugal SA	ADP Lavradio	?
40	Romania	Tirgu Mures	Azomures		1600
41	Romania	Slobozia	Amonil		1600
42	Romania	Slobozia	Amonil		
43	Romania	Craiova	Doljchim		?
44	Romania	Bacau Moldavia	Interagro Sofert		800
45	Romania	Turnu Magurele	Interagro Turnu		800
46	Romania	Fagaras	Nitramonia		?
47	Romania	Savinesti	Azochim		400
48	Serbia	Pancevo	HIP Azotara		?
49	Slovakia	Sala Nad Vahom	Duslo		1070
50	Spain	Palos	Fertiberia S.A.	Fertiberia Palos	1130
51	Spain	Puertollano	Fertiberia S.A.	Fertiberia Puertollano	600
52	UK	Hull	Kemira GrowHow UK Limited	Kemira Hull	815
53	UK	Ince	Kemira GrowHow UK Limited	Kemira Ince	1050
54	UK	Billingham	Terra Nitrogen (UK) Limited	Terra Billingham	1150
55	UK	Severnside	Terra Nitrogen (UK) Limited	Terra Core 1+2	800

The consortium supports EFMA's proposal to develop the emission benchmark curves from energy benchmark curves (including energy of feedstock, fuel and steam) by converting the energy benchmark curves by means of the actual plant specific emission factor (thus still calculating an emission benchmark). This approach has two advantages:

- The energy consumption of an ammonia plant accounts for all CO_2 emissions (process- and consumption-related), produced in the ammonia plant, regardless of whether there is a downstream utilisation or not. In this way plants without such downstream utilisation of carbon dioxide (e.g. urea production, CO_2 liquids for industrial purposes, CO_2 for food and beverage industry, etc.) are not disadvantaged.
- Plant Survey Institute (PSI) as consultant for ammonia plants has a lot of experiences in collecting energy consumption data from the operators and in developing energy benchmark curves.

The emission factor of heavier feedstocks is, due to its greater share of carbon, higher than that of lighter ones. Besides the fact that partial oxidation plants are more energy intensive than steam reforming plants, the higher emission factor leads to an even higher emission intensity. According to our principle "one product, one benchmark" no differentiation should be made between different feedstocks, fuels or techniques (see chapter 4.4.2 in the report on the project approach and general issues).

Furthermore no improvement factor accounting for production increases due to better technologies (upgrade, revamp) should be included in the allocation formula since such a factor is not be in line with the ex-ante principle on which the whole benchmark system is based. Larger production increases are to be handled in the framework of the new entrants reserve.

Regarding downstream utilizations the consortium proposes that the total number of allowances should be reduced by the CO_2 volume used as feedstock in a downstream urea plant or for other downstream utilization. This procedure is necessary because ammonia plant operators who operate a downstream unit utilizing CO_2 do not report the emissions which are attributed to the ammonia production, but the emissions after this downstream utilization. Not accounting for this circumstance, plant operators without such downstream utilization unit would be disadvantaged and there would be an allocation for not reported emissions being only temporarily stored and released afterwards.[5] This deduction should first happen from the free allowances (limited and determined by the benchmark) and then, if the amount of CO_2 for downstream utilization is higher than the free allowances, from the allowances to be bought in addition (determined by the actual CO_2 emissions). The deduction can never exceed the total CO_2 emissions, since the amount of CO_2 being downstream utilized is always lower than the total CO_2 emissions attributed to the ammonia production.

This deduction should happen ex-ante, what means that the allocated allowances are already reduced by the CO_2 volume. This approach would be in line with the ex ante benchmarking principle according to the amended Directive ("Transitional free allocation to installations should be provided for through harmonised Community-wide rules (ex-ante benchmarks)…"). The ex-ante principle calls for historical production figures and assumes that the CO_2 volume used for urea production is known from the past. The volume could be determined in the same way as the ammonia volume based on historical production.

EFMA objects that the market of downstream products was not stable and that the ex-ante would not account for this instability. However, for all products being included in the EU ETS the free allowances are determined on the basis of historical production, even though the market of all these products is not stable as well.

Furthermore, EFMA states, the ex-ante principle could result in an increased downstream production in order to decrease the actual CO_2 emissions and benefit from the free allowances. This could distort the downstream market towards the production of urea instead of ammonia nitrate, although the production of ammonia nitrate is under life cycle aspects

---

[5] The deduction could be avoided, if the monitoring and reporting guidelines were amended in that way, that the plant operators have to report all emissions which are attributed to the ammonia production including the CO_2 that is sold or used in urea production. Then, the CO_2 could be assigned to the ammonia installation both for determining the benchmark value and for the allocation without deduction. However, proposals for amending the monitoring and reporting guidelines are not within the scope of this report and according to the current monitoring and reporting guidelines, these emissions do not to have to be reported.

more environment friendly (less energy consumption). On the other hand, the market is determined by supply and demand which makes an overproduction of urea unprofitable. However, since the use of ammonia nitrate fertilizers can be partially substituted by urea fertilizers, this aspect is not to be neglected.[6]

There are two out of 35 ammonia plants belonging to EFMA with comparable low specific CO_2 emissions (two best plants in Figure 7 and Figure 8). Those plants are according to EFMA apparently integrated in larger industrial complexes which have a need for additional steam production capacity. The ammonia plants in those integrated sites can be designed to export large quantities of steam by:

- Import of electricity instead of installation of steam turbines
- Use of low-caloric steam on the site
- Overheating of low-caloric steam

According to EFMA the possibility to efficiently use the low caloric steam from ammonia production does not exist for the majority of installations.

The first bullet point describes the aspect of interchangeability of steam and electricity which occurs in the steam cracking process likewise. This issue probably applies at least to one out the two plants. This one has the 4th highest electricity consumption out of all 35 ammonia plants and at the same time the 2nd highest steam export.

The other plant has the highest steam export out of all 35 ammonia plants, but the electricity consumption is rather small. This plant probably falls in the last bullet point by producing 16 bar steam by overheating low-caloric steam. In general, good plant integration or the possibility to efficiently use the low caloric steam from ammonia production by upgrading it is no reason to exclude this plant from benchmarking, even if it is an exceptional case. The same holds for the ability to use the low caloric steam directly.

Furthermore it has to be clarified by the sector which reason (interchangeability of heat or steam and / or using of low caloric steam) contributes to the lowering of the energy consumption of a certain plant and to what extent. Up to now a clear differentiation is not given. **Whilst the interchangeability of heat and steam could give a reason to include electricity in the benchmark curve, the use of low-caloric steam by other production processes in the installation (outside the system boundary of ammonia production) is a plant specific technology which increases its efficiency and which should be rewarded. In order to follow our principle “one product, one benchmark” latter plants should not be excluded.**

According to EFMA the non-consideration of those two plants (out of 35) in the determination of the benchmark level increases its value by 11%. This increase should not be neglected, **if it was completely attributed to the interchangeability of steam and electricity**. Then, and only in this exceptional case, the electricity consumption should be

---

[6] Alternatively the deduction of allowances could be based on the actual CO_2 use in downstream utilizations during the trading period (e.g. at year end). However, such dynamic considerations are not within the scope of this report.

accounted for in the benchmark study, too. At this point we refer to chapter 6.3 in the report on the project approach and general issues, in which this approach is described.

5.2.2 Final proposal for products to be distinguished

The production of ammonia belongs to NACE code 20.15 and the PRODCOM number of ammonia is 20.15.10.75. For commercial use there are two different purities of ammonia: 99.5% and 99.9%. Whilst 99.5 ammonia is sufficient for most of the commercial uses, 99.9 ammonia is produced for the use as refrigerant agent. Ammonia leaving the ammonia plant is always 99.5 ammonia. The higher purity is obtained in a downstream distillation unit which does not belong to the perimeter. The use of ammonia as refrigerant agent is very small. Most of the ammonia is used as on-site feedstock for nitric acid, ammonium nitrate, urea, NPK fertilizers and ammonia salts as well as N-containing organic chemicals. Another downstream process is the production of ammonia in aqueous solution (PRODCOM no. 20.15.10.77). However, all these downstream processes do not belong to the ammonia production.

5.3 Benchmark values

5.3.1 Background and source of data

The fertilizer industry, which is represented by EFMA, is regularly carrying out energy benchmarking of ammonia plants in Europe and on a global basis, using the independent Plant Survey Institute (PSI). EFMA represents altogether 35 out of about 55 European ammonia plants. The benchmarking is based on a simple methodology covering all direct and steam inputs and outputs for ammonia plants. The specific emissions are calculated by accounting for the exact composition of the feed and fuel sources, and using the standard assumptions for the CO_2 content of the steam use. A benchmarking study including the 35 EFMA plants and based on the years 2007-2008 has been carried out by PSI for establishing the average of the 10% best performers. Those data (including benchmark curves) are available to the consortium.

5.3.2 Final proposed benchmark values

The Best Available Techniques for existing plants as defined by the EU Commission has a net energy consumption of 27.6- 31.8 GJ / t ammonia. From PSI's global benchmarking 2006-2007 the EU BAT covers some 10% of the best performers. The average energy consumption in Europe was 35.7 GJ / t NH_3 and at the world level 36.6 GJ / t NH_3. The following figures show the outcome of the latest benchmarking study for the years 2007-2008:

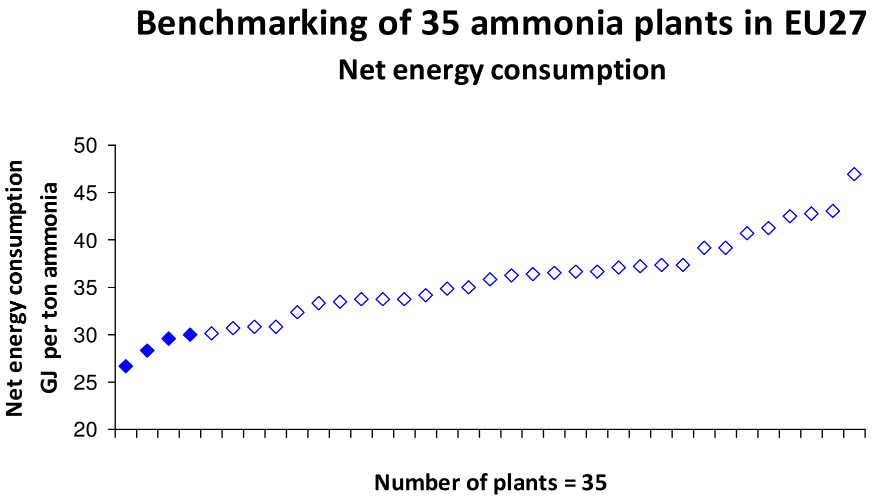


Figure 6 Energy benchmark curve including all 35 European EFMA plants and the inputs feed, fuel and steam (EFMA 2009a)

Figure 6 shows the specific energy consumption of the European EFMA plants (including energy of feedstock, fuel, steam and electricity). The best plant has a specific energy consumption of about 27 GJ / t NH_3. The specific energy consumption of the average best 10% of all plants is 28.7 GJ / tNH_3.

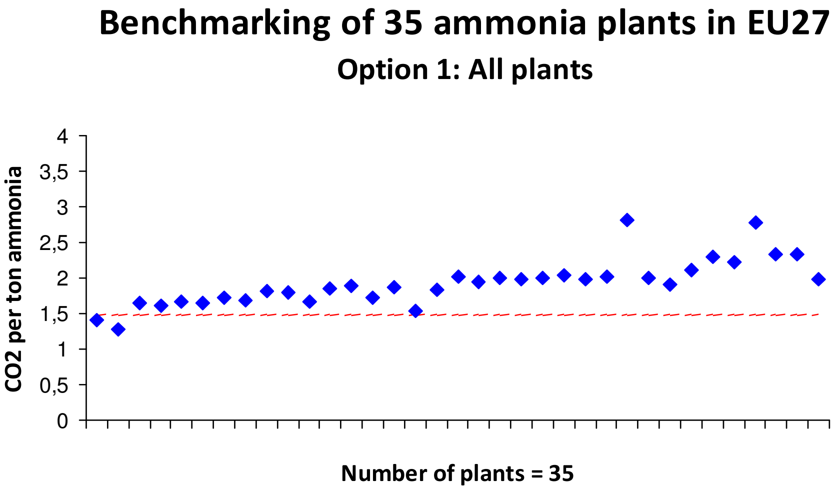


Figure 7 CO_2 benchmark curve including all 35 European EFMA plants (EFMA 2009a)

Multiplying the energy intensity of every plant in Figure 6 with the plant specific emission factor results in the emission benchmark curve (Figure 7). **For this calculation the electricity consumption is <u>not</u> included.** The order of the plants in Figure 7 is the same as in Figure 6, what does not result in an increasing curve. This shows that a plant with good emission intensity is not necessarily a good plant regarding the overall energy intensity (e.g. plant no. 16). In order to account for the overall efficiency (including electricity) in determining the benchmark level, EFMA did not reorder the plants. The average best 10% benchmark value is 1.48 t CO_2 / t NH_3.

However, this procedure is not in line with the amended Directive calling for benchmarking greenhouse gas efficiency. To meet this requirement the data points in Figure 7 have to be ordered from the less to the most emission intensive plant to get an increasing curve. Doing this the benchmark value would lower to **1.46 t CO_2 / t NH_3**, which is the recommended preliminary benchmark value in this study.

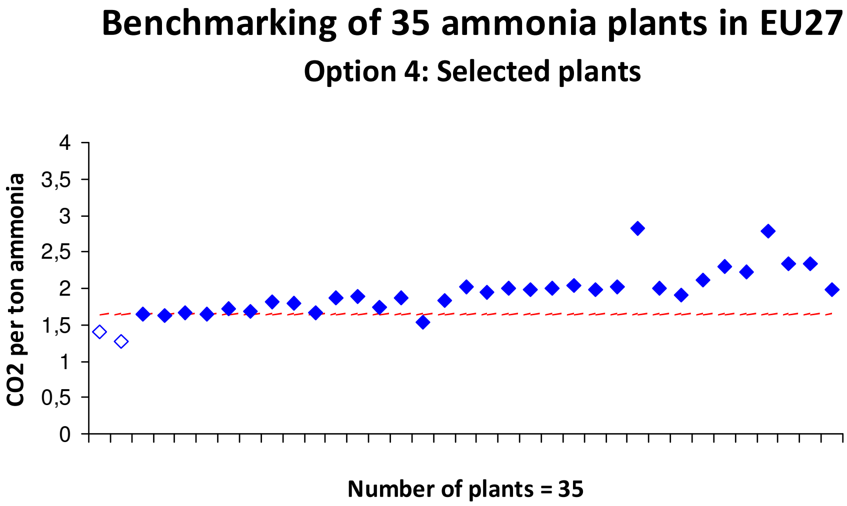


Figure 8 CO_2 benchmark curve excluding those two plants which export large quantities of steam (not blue filled quads) from the 35 European EFMA plants (EFMA 2009a)

The third benchmark curve (Figure 8) excludes the two plants importing large quantities of electricity / using low-caloric steam what results in a benchmark value of 1.64 tCO_2 / tNH_3. At this point it should be mentioned again, that an exclusion is only justifiable, if the lower CO_2 emissions can be attributed to the interchangeability of heat and steam. However, this issue has to be further investigated. Furthermore, the order of the plants has to be changed from the less to the most emission intensive plant. Then the benchmark value is **1.61 tCO_2 / tNH_3**.

At this point it is mentioned, that the non-EFMA plants are situated in large part in the new EU27 states. According to EFMA those plants are less emission efficient than the EFMA members and would therefore not be within the best 10% plants and not influence the benchmark value considerably. If they were included, the benchmark would be based on the average of the best 6 plants instead of the average best 4 plants. The benchmark difference is small.

5.3.3 Possibility of other approaches

There are no reasons for other approaches.

5.4 Stakeholder comments

EFMA advocates the use of net energy consumption (GJ/t ammonia) as basis for establishing emission allowances. This will avoid a competitive distortion from temporary short-term capture of CO_2 in downstream products (urea, industrial CO_2, etc). EFMA argues that the annual emission allowance should not give rise to taking advantage of such short-term capture, and that due to fluctuations in annual consumption levels the CO_2 used for short-term capture should be deducted as non-tradable emissions at the end of the year.

EFMA suggests that the allowances are allocated based on the total CO_2-formation from feed+fuel and that the CO_2 that is actually being utilised in downstream products, should be turned in as emissions at every years end (ex post instead of ex ante) towards the emission allowance. EFMA advocates that CO_2 available in pure form from an ammonia plant is an ideal source for starting carbon capture projects in Europe. This permanent capture of CO_2 should be promoted also as alternative of the short term capture in urea and industrial gas applications. CO_2 consumed in urea is unavailable for carbon capture.

EFMA believes the inclusion of a carbon factor (CO_2/GJ) <u>in the allocation formula</u> should be accounted for to reflect different feedstocks. Such a carbon factor accounts for the use of e.g. residues as feedstock.

$$Allowances = \\ Benchmark\,(2007/2008)\left[\frac{GJ}{tNH_3}\right]\times Emission\ factor\left[\frac{tCO_2}{GJ}\right]\times historical\ Production\,[tNH_3]$$

Equation 11

Since ammonia is a globally traded commodity, EFMA strongly advocates that the benchmark should be the global 10% best performer, and not the average of the European 10% best.

Plants based on heavy fuel oil would normally have stringent environmental treatment of the waste effluents and gas emissions. Plants with such clean 'incineration' of waste fuel products should have a special treatment for CO_2 allowances, so that they are not made economically unsustainable.

Existing production plants are continuously being modified and optimised for increased production. Hence, the annual production volume in the allocation formula should be granted a growth factor to account for such improvements.

On the first of July DG Enterprise presented in a Stakeholder Consultation their results of the assessment of the sectors having the risk of carbon leakage. The fertilizer Industry is highest on that list (carbon intensity Costs / GVA = 92.4% and Trade exposure =27.4%) meaning serious risk of carbon leakage. Carbon leakage (Closure of fertilizer plants in Europe and dependence on imports of fertilizers from outside Europe) will seriously affect food supply in Europe.

Setting very stringent baseline levels (average 10% best performing plants) will surely not contribute to diminishing this risk of carbon leakage.

EFMA has calculated its costs for complying with a benchmarking approach and conclude that the benchmark for ammonia plants should be at a relative BM level of at least 118 (100 corresponds to the average best 10% benchmark level).

When producing ammonia, a major part (approx 70%) of the generated CO_2 is clean and can be used for other purposes, such as for the production of urea fertilizers, CO_2 liquids for industrial use and in the food and beverage sector, or for methanol and other by-products. This is a short term temporary capture of CO_2 and can give rise to competitive distortion in the context of emission allowances, as exemplified below:
There are two basic types of nitrogen fertilizers: Urea and Ammonium Nitrate. In a life cycle perspective (production and use), ammonium nitrate has an advantage over urea with respect to agronomic efficiency, profitability for the farmer, and environmental emissions including overall GHG emissions (from factory and soil). However, when considering only the production part, urea will have an advantage regarding GHG emissions from the factor stack, since part of the CO_2 from the ammonia plant is captured (short term) in the urea, but released again as soon as the product is used on the farmer's field. When manufacturing ammonium nitrate, all the CO_2 of the ammonia plant is released at the factory. Hence, for a fair CO_2 allocation to ammonia plants, it is important to base the allocation on the total generated CO_2 emission, and not on the emissions from the factory stack. This will avoid giving ammonia / urea producers an unfair advantage.
This discrepancy can be accounted for by giving allowances based on the historical production of the various downstream products and allocating the CO_2 emissions accordingly. However, this can also lead to a distortion. For example, a producer of ammonium nitrate will be granted high emission allowances for its ammonia plant, but will have the incentive to move to urea or develop other means of temporary capture of CO_2, thus making it possible to generate windfall profits without really having reduced the CO_2 emission in a life-cycle perspective. The only means of CO_2 capture that should be recognised would (with today's knowledge) be permanent carbon capture and storage in the ground. In this respect, the ammonia / ammonium nitrate production route offers the best opportunity since some 70% of the CO_2 is clean and ready for capturing. This is not the case in the ammonia / urea route since the clean CO_2 will be released on the farmer's field.
To avoid competitive distortion and to avoid undesired incentives for short-term capture of CO_2, EFMA suggests that the emission allowance for ammonia plants should be based on the total generated CO_2 (as calculated from specific energy consumption data), and that the CO_2 that is temporarily captured should be considered as released from the ammonia plant, and to be accounted for on an annual basis along with the CO_2 that is released directly.
We suggest regarding ammonia plants with unusually high steam export of more than 5 GJ / t NH_3 as outliers. These installations shall not be used in the benchmark for the allocation of free certificates under ETS.

A small number of ammonia plants (2 of 35 in the EFMA Benchmark, see Figure 7: the best two plants) are apparently integrated in larger industrial complexes with a need of additional steam production capacity. Such plants can be designed to export large quantities of steam by:
- Import of electricity instead of installation of steam turbines
- Use of low-caloric steam on the site

- Overheating of low-caloric steam
- etc.

The possibility to efficiently use the low caloric steam from ammonia production does not exist for the majority of installations.

The existing PSI-Benchmark was designed to rank ammonia plants according to their energy efficiency. For this purpose, the use of a single conversion factor for steam generation was suitable and generally accepted.

This is not the case if the benchmark is used to allocate certificates. For an ammonia plant with a highly efficient steam generation, this fixed conversion factor will calculate an unrealistically high energy credit for steam, resulting in unrealistically low net energy consumption for ammonia. This effect escalates with increasing steam export.

For ammonia plants: The CO_2 benchmark level should be lifted to the emission level in natural gas based plants with an energy efficiency of 31.8 GJ / t of ammonia. This is recognised as the Best Available Technique for existing plants, and belongs to the 10% best worldwide.

5.5 Additional steps required

The actual benchmark curves include 35 out of 55 ammonia plants in the European Union. The 20 missing plants are not represented by EFMA and so no data are available up to now. Those plants are situated exclusively in the Eastern EU members and have been invited by EFMA to participate in the benchmarking. That raises the question how information can be collected from those plants. To cover all plants in the EU they have to be included. However, EFMA assumes that the emission intensity of those plants is comparatively higher than those of the EFMA members. That is why those plants will influence the benchmark level only to a lesser extent (compare average best 4 and average best 6 plants in Figure 6).

6 Adipic acid

6.1 Production process

In Europe there are only 5 adipic acid installations which account for 13 Mt CO_2 emissions (CO_2-equivalents). A sixth plant in UK was shut down recently. The production of adipic acid is therefore on position 4 of the most emission intensive processes in the European chemical industry (see Table 3 in Chapter 2). The following table lists all locations of adipic acid plants as well as their capacity and operator:

Table 8 Adipic acid installations EU27 and capacities (Chemplan 2009)

Country	Company	Location	Capacities (t/yr)
France	Rhodia-S.A.	Chalampé	320
Germany	BASF	Ludwigshafen	260
	Lanxess	Krefeld-Uerdingen, Leverkusen	68
	Radici Chimica (technology: Krupp Uhde)	Zeitz, Tröglitz, Saxony-Anhalt	80
Italy	Radici Chimica	Novara	70

Adipic acid is commercially manufactured by the catalytic oxidation of KA-oil (cyclohexanone / cyclohexanol mixture or also called Ketone-Alcohol oil) by using excess of strong nitric acid. The KA-oil can either be produced on-site by oxidation of cyclohexane or the hydrogenation of phenol or be imported from external producers.

The reactor, controlled at 60 – 80 °C and 0.1 – 0.4 MPa, is charged with the recycled nitric acid stream, the KA feed material and makeup acid containing 50-60% nitric acid and copper-vanadium catalysts. NO_x is stripped with air, giving a waste gas stream. Water is removed from the reaction mixture by distillation giving a waste water stream. Adipic acid is isolated and purified by a two-stage cristallisation / centrifugation and washing with water. The chemical structure of adipic acid and the chemical reaction is as below:

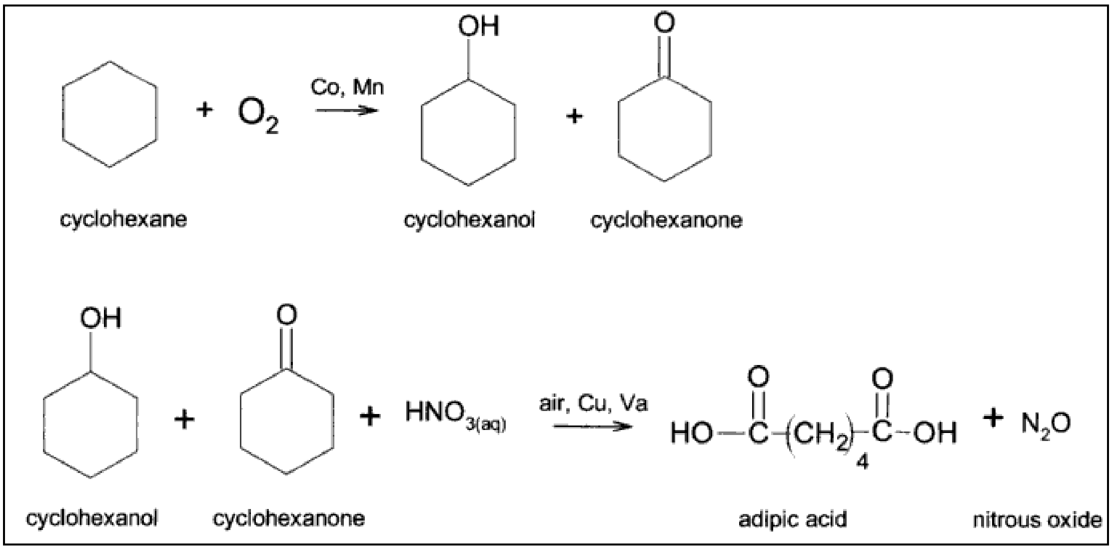


Figure 9 Chemical reactions in the adipic acid production (CEFIC 2009d)

The heat of reaction (6.280 MJ/kg) is more than high enough to provide the energy to heat the inputs to the reaction temperature. Distillation however needs a lot of thermal energy. Adipic acid is obtained in a yield greater than 90%. Higher ketone content results in increased N_2O generation, whereas higher alcohol content results in less N_2O generation (IPCC 2001).

Nitrous oxide is formed by further reaction of the nitrogen-containing products of nitrolic acid hydrolysis. The NO and NO_2 are reabsorbed and converted back to nitric acid. However, N_2O cannot be recovered in this way and is therefore the major by-product of the process.

Emissions and by-products

From the reaction it is evident that there is 1 mol of N_2O produced per mol of adipic acid which corresponds to approx. 300 g N_2O / kg adipic acid. The IPCC default emission factor is 270-300 kg N_2O / t of adipic acid. Other by-products are CO, CO_2, non-methane volatile organic compounds (NMVOC) and some lower dicarboxylic acids (glutaric acid and succinic acid).
N_2O emissions also depend on the catalyst type, catalyst age, metal gauze type and reactor operating conditions. Catalyst replacement should be done periodically because older catalysts will not be as efficient as newer catalysts and thus lead to higher N_2O emissions.

N_2O rich off-gas can be re-used in two ways:
1) By burning it at high temperatures in the presence of steam to manufacture nitric acid (this utilises the N_2O off-gas and also avoids the N_2O generated in nitric acid production).
2) By using N_2O to selectively oxidise benzene to phenol.

Sometimes adipic acid is not dried but used as liquid solution for other downstream processes. That implies that the specific energy consumptions is a bit lower than for the dried adipic acid, but all the producers refer to dried adipic acid as standard product which is the major marketable end product, resulting from several energy-intensive processes like crystallisation, washing and drying.

Confidentiality of data due to the limited number of installations is an important constraint for harmonized benchmarking of adipic acid product. Abatement technology has already been implemented since 1997 leading to more than 90% reduction in N_2O emissions. This can be seen from the following graph.

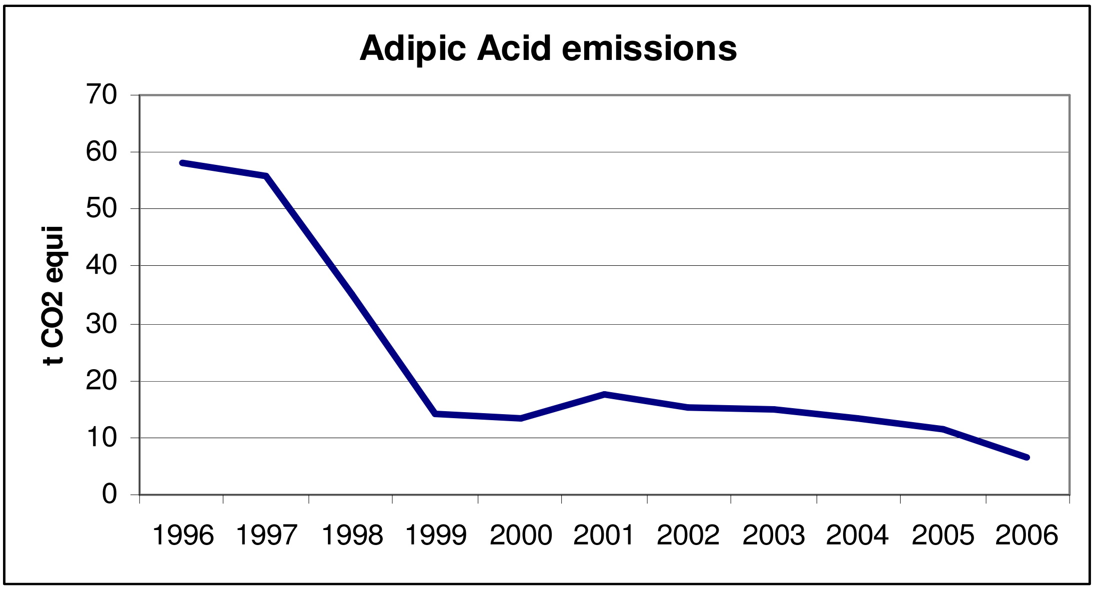


Figure 10 N_2O reductions achieved over the last 10 years in Europe (CEFIC 2009d)

As per Cefic, all installations are equipped with abatement technologies in Europe today. Although abatement technologies for N_2O emissions from adipic acid plants are already largely installed there is still some scope of further improvement.

A questionnaire was sent out by Cefic to adipic acid producers, which covers all mass and energy streams inside the battery lines. Summary results were provided to Fraunhofer ISI.

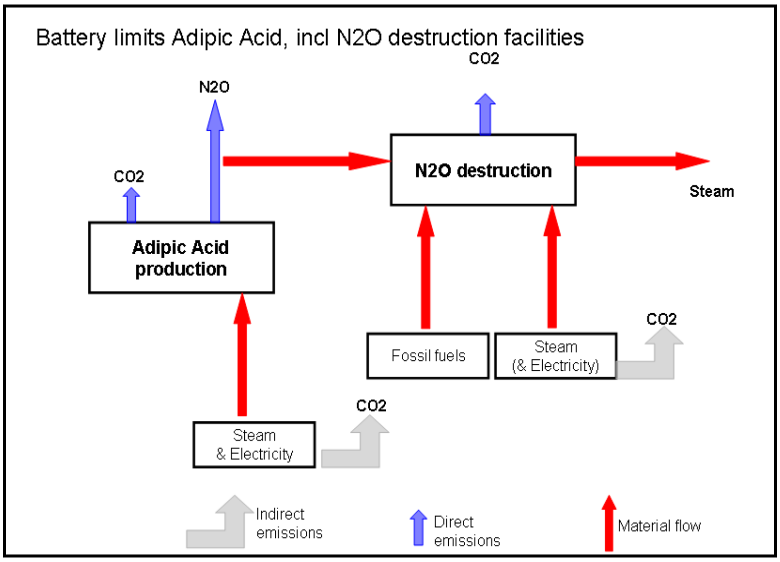


Figure 11 Boundaries of the N_2O benchmarking (CEFIC 2009d)

Below are the summarized emissions for all the installations within EU-27 (total emissions including process emissions in CO_2 equivalents and indirect CO_2 from utilized steam without electricity):

Table 9 Summarised N_2O emission (CEFIC 2009d)

N_2O or CO_2 eq emission from adipic acid plants	**2005**	**2007/08[1]**
Total emissions (million t CO_{2eq})	13.00	-
- Weighted average (t CO_{2eq} / t adipic acid)	13.76	10.82
Results excluding steam and electricity (million t CO_{2eq})	12.50	-
- Weighted average (t CO_{2eq} / t adipic acid)	13.07	10.27
Results for steam only (million t CO_2)	0.50	-
- Weighted average (t CO_2 / t adipic acid)	0.51	0.40

[1] one plant (Invista, UK) was not covered for data from 2007/08

(-) total value not given due to confidentiality of data from the excluded Invista-plant

N_2O abatement methods (end of pipe technologies):

1) Catalytic destruction of N_2O (destruction factor 90 – 95%): this method uses metal oxide catalysts (e.g. MgO) to decompose the N_2O into N_2 and O_2. Heat from the strongly exothermic reaction may be used to produce steam. Catalyst typically needs to be replaced twice a year.
2) Thermal destruction (destruction factor 98 – 99%): this involves combustion of the off-gases in the presence of methane. The N_2O acts as an oxygen source and is reduced to nitrogen, giving emissions of NO and some residual N_2O. The combustion process can be used to raise steam. The heat of N_2O decomposition, combined with fuel energy, helps providing low-cost steam.

Partial recycling of N_2O to manufacture nitric acid can be a cost-effective option in some circumstances. Recovery of waste heat from the exothermic abatement reactions is more effective with thermal systems due to their higher operating temperatures, but producers report that only about 60% of the operating cost may be recovered through steam generation. More efficient systems can cover more of the operating costs or may actually provide a marginal net cost saving.

6.2 Benchmarking methodology

6.2.1 Background

Even though abatement techniques abate 90% or more of N_2O emissions from adipic acid plants, they ranked on the 4th place on the table of top greenhouse gases emitters Europe wide. As there are only 5 plants in the EU-27, it is not easy to calculate the benchmark level with the method of the average of the 10% best installations because the best 10% will be only one plant and the benchmark value could not be established due to obvious data confidentiality. To develop the benchmarking level we need to consider the performance of at least three plants, because if one takes the average of the best two performers than confidentiality will also be a problem because one of those two will know each others data. An alternative it to base a benchmark value on an assumed abatement percentage. It is this route we take below, pending on further discussion regarding confidentiality in the benchmark curve.

6.2.2 Final proposal for products to be distinguished

The production of adipic acid belongs to NACE code 20.14 and the PRODCOM number is 20.14.33.850 (adipic acid; its salts and esters).

Sometimes adipic acid is not dried but used as liquid solution for other integral processes. We propose to use solid adipic acid as the standard product which is the major marketable end product, which results from several energy intensive processes like crystallisation, washing and drying.

6.3 Benchmark values

6.3.1 Background and source of data

CEFIC has been continuously carrying out the benchmark study for the adipic acid since April 2009. They have compared the emissions data from 2005 with respect to 2007/08 while lately one installation (Invista, UK) was closed in 2008.

6.3.2 Final proposed benchmark values

As a starting point the consortium proposes a benchmark value of **5.6 t CO_2-equivalents / t adipic acid** corresponding to a 94% abatement efficiency. This value is given as lowest efficiency for the implementation of abatement techniques in existing adipic acid plants (BREF – LVOC, 2003). Furthermore, 5.6 t CO_2-equivalents / t adipic acid are the lowest achieved specific CO_2 emissions of the German adipic acid plant from 2001-2007 (see Table 10). This plant is equipped with an abatement technique. The values are calculated by dividing the yearly production figures for Germany (t adipic acid) (PRODCOM 2009) by the yearly emissions from the adipic acid production in Germany (kt CO_2-equivalent) (UNFCCC 2009).

Table 10 Specific CO_2 emissions for the German adipic acid plant in from 2001-2007

	2001	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**
kt CO_2-eq.	3690	3848	3778	4781	3276	3004	5624
t adipic acid	367095	428707	-	376916	476572	545665	543665
t CO_2-eq. / t adipic acid	10.1	9.0	-	12.7	6.9	5.6	10.3

According to Cefic an abatement efficiency between 94 and 98% (BREF – LVOC, 2003) is not realistic because of start ups, shut downs, emergency shut downs and transient periods of the abatement plants. That is why Cefic proposes 8.37 t CO_2-equivalents / t adipic acid as benchmark for the production of adipic acid, what corresponds to a 90% efficiency of the abatement technique (CEFIC 2009e). The CO_2 emissions from steam which is used for drying the adipic acid are included.

It is reasonable to compare the Cefic proposal with the result obtained when applying the abatement proposed in the reference document on BAT (BREF) notes. Assuming an average emission factor of 300 kg N_2O / t adipic acid (IPCC 2001) and an abatement efficiency of 98% would result in 1.8 t CO_2-equivalents / t adipic acid (300 kg N_2O / t adipic acid x (1-0.98) x 310 kg CO_2-equivalents / kg N_2O=1800 kg CO_2-equivalents / t adipic acid.

6.3.3 Possibilities of other approaches

Initially Cefic suggested developing one benchmark for all installations by mathematical average of the best three plants. At present, no data for specific plants were available to us to judge on this suggestion.

6.4 Stakeholder comments

Small number of installations (5) and producers (4) makes it impossible to apply standard methodology of 10% best due to confidentiality and competition policy.

All production installations have abatement technology installed which in theory delivers similar results, but the reliability of the abatement system does not allow reaching technical limit values of 95-98% abatement.

It is necessary to have the adipic acid production and N_2O abatement system perfectly in line all year round in order to achieve the limit values. That cannot be possible in all situations like start up, shut down, emergency shut down and transient period. It is important to focus firstly on the safe operation of the plant and then on abatement. Therefore we cannot approve the very high value of the LVOC BREF which claims and overall abatement level of 95-98% when applied to existing technology.
The sector has already achieved significant improvements over recent year (almost 90% reduction in N_2O emissions) and therefore values of today can be considered as technologically very advanced or even at the limit.
In comparison to the average value, 90% abatement represents -21.7% improvement, which is fully in line with the goal of the European Union to reduce the overall GHG emissions to at least below 1990 levels by 2020.

In line with this analysis the Adipic Acid group proposes **8.37 t CO_2 / t Adipic Acid** as benchmark for the Adipic Acid producers, which represent a 90% efficiency in abatement.

6.5 Additional steps required

The benchmark curve was not provided by Cefic, so far, due to data confidentiality. The curve with the actual values would be useful in estimating relative benchmark levels and the spread factor and allow for a more reliable analysis.

7 Hydrogen and Synthesis gas

7.1 Production process

The term “synthesis gas” (syngas) means not a certain mixture of carbon monoxide (CO) and Hydrogen (H_2) but covers the range between pure CO and pure H_2. According to BASF, an average chemical product has a H_2:C ratio of 1.8.

There are 83 installations[7] which will be included in the EU ETS from 2013 (roads2hycom 2007). It is important to mention that there are installations both in the chemical and in the refinery sector. There are four possibilities where and by whom the syngas / H_2 is produced:

- Captive within the chemical sector
- Gas producers supplying the chemical industry
- Gas producers supplying refineries
- Captive within the refinery sector

While the first three bullet points describe the production of synthesis gas / H_2 within the chemical sector as defined in PRODCOM, the last bullet point describes the production in the refinery sector.
The following table list all 83 hydrogen plants in the EU:

Table 11 Hydrogen plants in the EU (roads2hycom 2007)

No.	Country	Location	Operator	Plant	Capacity [km³/d]
1	Austria	Linz-Wels	Linz	VAI Siemens	1763
2	Belgium	Arr. Gent	Zelzate	Sidmar	1625
3	Belgium	Arr. Liège	Seraing	Arcelor	1025
4	Belgium	Antwerpen	Antwerpen	BASF	416
5	Belgium	Antwerpen	Antwerpen	Fina Antwerp Olefins	744
6	Belgium	Antwerpen	Antwerpen	BASF	301
7	Belgium	Antwerpen	Antwerpen	Air Liquide	2160
8	Belgium	Antwerpen	Antwerpen	Air Liquide	2160
9	Czech Republic	Moravskoslezsky kraj	Ostrava	Moravske Chemicke Zavody a.s.	320
10	Denmark	Vestsjællands amt	Kalundborg	Statoil	473
11	Finland		Raahensaio	Ruuki	762.5
12	France	Bouches du Rhône	Lavéra	Naphtachimie SA	385
13	France	Bouches du Rhône	Fos sur Mer	Sollac	1875
14	France	Haut Rhin	Chalampe	Linde	500
15	France	Moselle	Carling St Avold	Total	286

---

[7] Methanol plants included, ammonia plants excluded

Continuation Table 11

No.	Country	Location	Operator	Plant	Capacity [km³/d]
16	France	Pyrénées-Atlantiques	Pardies	Pardies Acetiques SA, Acetex Chimie	512
17	France	Rhône	Saint Fons	Air Liquide	360
18	France	Seine Maritime	Port Jérôme	Air Liquide	1200
19	Germany	Bottrop, Kreisfreie Stadt	Bottrop	Prosper	2500
20	Germany	Cottbus, Kreisfreie Stadt	Schwarze Pumpe	Lautsitzer Analytik	460
21	Germany	Duisburg	Duisburg (Schwelgern)	Uhde	3300
22	Germany	Duisburg	Duisburg (Huckingen)	HKM	1375
23	Germany	Erfkreis	Wesseling	Shell & DEA Mineraloel	1726
24	Germany	Gelsenkirchen, Kreisfreie Stadt	Gelsenkirchen	Ruhr Oel	997
25	Germany	n/a	Dilligen	Zentralkokerei Saar	1625
26	Germany	Salzgitter, Kreisfreie Stadt	Salzgitter	Salzgitter Flachstahl	1875
27	Germany	Stade	Stade	Air Liquide	350
28	Germany	Stade	Stade	Dow	1100
29	Germany	Bonn, Kreisfreie Stadt	Köln	BP	599
30	Germany	Dithmarschen	Brunsbüttel	Linde	480
31	Germany	Erfkreis	Wesseling	Basell Polyolefine	531
32	Germany	Ingolstadt, Kreisfreie Stadt	Ingolstadt	BAYERNOIL Raffineriegesellschaft mbH	2350
33	Germany	Leverkusen, Kreisfreie Stadt	Leverkusen	Bayer AG	290
34	Germany	Ludwigshafen am Rhein, Kreisfreie Stadt	Ludwigshafen	BASF	323
35	Germany	Ludwigshafen am Rhein, Kreisfreie Stadt	Ludwigshafen	BASF	922
36	Germany	Ludwigshafen am Rhein, Kreisfreie Stadt	Ludwigshafen	BASF	1300
37	Germany	Merseburg-Querfurt	Leuna	Linde	1000
38	Germany	Neuss	Dormagen	Bayer AG	333
39	Germany	Recklinghausen	Marl	ISP Marl	326
40	Italy	Ancona	Falconara Marittima	Api Energia SpA	400
41	Italy	Cagliari	Sarroch	Sarlux SpA; joint-venture between Saras SpA and Enron Corp.	480
42	Italy	Livorno	Piombino	Lucchini	774
43	Italy	Mantova	Mantova	Air Products	425
44	Italy	Mantova	Mantova	EniChem	362
45	Italy	Savona	San Giuseppe di Cairo	Italiana Coke	674

Continuation Table 11

No.	Country	Location	Operator	Plant	Capacity [km³/d]
46	Italy	Siracusa	Priolo	Air Liquide	650
47	Italy	Siracusa	Priolo	Polimeri Europa	427
48	Italy	Venezia	Porto Marghera	EniChem	540
49	Italy	Venezia	Porto Marghera	Italiana Coke	315
50	Netherlands	Agglomeratie Haarlem	IJmuiden	Corus	2663
51	Netherlands	Agglomeratie's-Gravenhage	Botlek-Rotterdam	Akzo Nobel	500
52	Netherlands	Agglomeratie's-Gravenhage	Botlek-Rotterdam	Lyondell Chemical	383
53	Netherlands	Delfzijl en omgeving	Delfzijl	Methanor	3400
54	Netherlands	Groot-Rijnmond	Rozenburg	Air Liquide	288
55	Netherlands	Groot-Rijnmond	Rozenburg	Air Liquide	326
56	Netherlands	Groot-Rijnmond	Rozenburg	Air Products	487
57	Netherlands	Noordoost-Noord-Brabant	Moerdijk	Shell Chemicals	468
58	Netherlands	Noordoost-Noord-Brabant	Moerdijk	Basell	341
59	Netherlands	Overig Zeeland	Bergen op Zoom	Air Liquide	744
60	Netherlands	Zeeuwsch-Vlaanderen	Terneuzen	Dow	885
61	Netherlands	Zeeuwsch-Vlaanderen	Terneuzen	Dow	603
62	Netherlands	Zuid-Limburg	Geleen	Sabic EuroPetrochemicals	643
63	Spain	A Coruña	La Coruña	Air Liquide	760
64	Spain	Asturias	Aviles	Aceralia	1598.75
65	Spain	Asturias	Gijon	Aceralia	1250
66	Spain	Cantabria	Torrelavega	Solvay	1440
67	Spain	Castellón	Castellon de la Plana	Compania Espanola de Petroleos	657
68	Spain	Ciudad Real	Puertollano	Air Liquide	1170
69	Spain	Tarragona	Tarragona	Dow	297
70	Spain	Tarragona	Tarragona	Repsol	312
71	Sweden	Norrbottens län	Lulea	SSAB	863
72	Sweden	Stockholms län	Oxelosund	SSAB	538
73	Sweden	Västra Götalands län	Stenungsund	Borealis	318
74	United Kingdom	Bridgend and Neath Port Talbot	PortTalbot	Corus	1825
75	United Kingdom	City of Kingston upon Hull	Hull	BP	576
76	United Kingdom	Clackmannanshire and Fife	Mossmorran	ExxonMobil Chemical	416
77	United Kingdom	Falkirk	Grangemouth	BP	531
78	United Kingdom	Halton and Warrington	Runcorn	INEOS Chlor	546
79	United Kingdom	Hartlepool & Stockton-on-Tees	North Tees	BOC	978

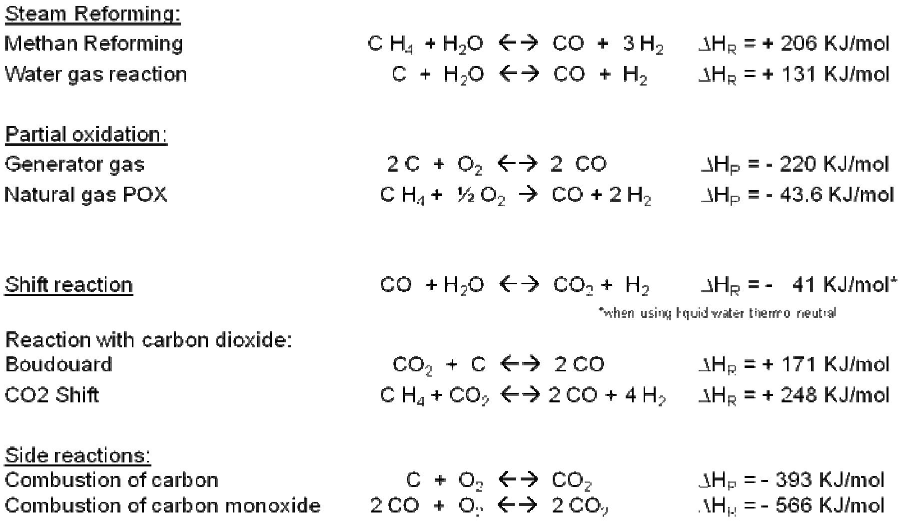
Continuation Table 11

No.	Country	Location	Operator	Plant	Capacity [km³/d]
80	United Kingdom	North and North East Lincolnshire	Scunthorpe	Corus	1663
81	United Kingdom	North and North East Lincolnshire	Scunthorpe	Corus	1662.5
82	United Kingdom	South Teesside	Wilton	Huntsman Petrochemicals Ltd.	450
83	United Kingdom	South Teesside	Teesside	Corus	2500

The production processes to produce syngas / H_2 are similar compared to the initial step in the ammonia production:

- Steam reforming
- Partial oxidation

Both processes are described in chapter 5.1. There is a large spectrum of usable feedstocks (solid, liquid and gaseous, for example petroleum coke (resulting in a synthesis gas with a H_2:CO ratio of 0.6), vacuum residues (H_2:CO=1:1) and natural gas (H_2:CO=2:1)). The H_2:CO ratio can be increased by the shift reaction.



Steam Reforming:
Methan Reforming $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $\Delta H_R = +206$ KJ/mol
Water gas reaction $C + H_2O \leftrightarrow CO + H_2$ $\Delta H_R = +131$ KJ/mol

Partial oxidation:
Generator gas $2C + O_2 \leftrightarrow 2CO$ $\Delta H_P = -220$ KJ/mol
Natural gas POX $CH_4 + ½O_2 \rightarrow CO + 2H_2$ $\Delta H_P = -43.6$ KJ/mol

Shift reaction $CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H_R = -41$ KJ/mol*
*when using liquid water thermo neutral

Reaction with carbon dioxide:
Boudouard $CO_2 + C \leftrightarrow 2CO$ $\Delta H_R = +171$ KJ/mol
CO2 Shift $CH_4 + CO_2 \leftrightarrow 2CO + 4H_2$ $\Delta H_R = +248$ KJ/mol

Side reactions:
Combustion of carbon $C + O_2 \leftrightarrow CO_2$ $\Delta H_P = -393$ KJ/mol
Combustion of carbon monoxide $2CO + O_2 \leftrightarrow 2CO_2$ $\Delta H_R = -566$ KJ/mol

Figure 12 Important conversion reactions from feedstock to syngas (BASF 2009a)

7.2 Benchmarking methodology

7.2.1 Background

The European Industrial Gases Association (EIGA) and Cefic presented briefly in a meeting on 16 June at the Fraunhofer Institute their views on the way hydrogen could be treated. Two key options for determining benchmarks for hydrogen can be distinguished:

1. A first benchmark based on an assessment of “on purpose” hydrogen plants[8] that are operated by other companies / installations than refineries and a second benchmark based on the refinery proposed CWT approach[9] (complexity-weighted-t).
2. Directly following a uniform approach. Given the fact that an approach for hydrogen in the CWT approach for refineries is already there, it is the most logical choice to follow this approach.

EIGA / Cefic proposes to follow the second option for three reasons:

- Following the same approach for all “on purpose” hydrogen plants ensures equal treatment for those units and avoids distorting competition for hydrogen production between the refinery and the chemical sector.
- About 80% of all “on purpose” hydrogen production is used in refineries
- Following an existing approach (i.e. the one for refineries) is more easy and straightforward to implement.

We propose to use the CWT approach for all on purpose hydrogen production units except for ammonia production, which can be seen as an independent group of installations in which hydrogen and ammonia production is fully integrated. Hydrogen produced as by-product by other production processes (e.g. steam cracking) is not part of this methodology.

The CWT approach was developed by the refiners – represented by CONCAWE - in association with Solomon Associates, a consultant of the refinery sector. This model is a benchmarking methodology for broad refinery operation and contains implicit hydrogen benchmarks, since the hydrogen production is one of various refinery units (besides e. g. crude distillation columns, catalytic reformers, alkylation units and others, so called “functions” in the model). To obtain a refinery’s CWT, for each process unit within the refinery a CWT factor is assessed which is a measure of the average CO_2 intensity for the process unit relative to the basic process of crude distillation. The CWT factor is multiplied by the throughput for each single process type unit to calculate the CWT for that special process type. For this calculation detailed activity data of every unit are required. The refinery total CWT is the sum of the CWTs of all process units plus an incremental CWT for non-process facilities such as storage tanks. At this point we refer to the sector report for the refineries, where the CWT approach is explained in detail.

---

[8] Excluding units with hydrogen as by-product and excluding ammonia plants.

[9] For a detailed description of the CWT approach see sector report for the refinery sector.

To derive an implicit benchmark for the H_2 installation, the CWT factor is multiplied with a benchmark value (t CO_2 / CWT). This benchmark is determined based on an assessment at refinery level, not at unit level, taking into account the specific carbon dioxide emissions of the population of European refineries. This method should be applied for hydrogen producing units regardless of whether these units are within or outside the refinery sector.

The CWT approach currently contains four different CWT functions for the production of hydrogen / Syngas:

1. Hydrogen production, gas feed
2. Hydrogen production, liquid feed
3. Partial Oxidation Syngas for hydrogen and methanol
4. Partial Oxidation Syngas for fuel

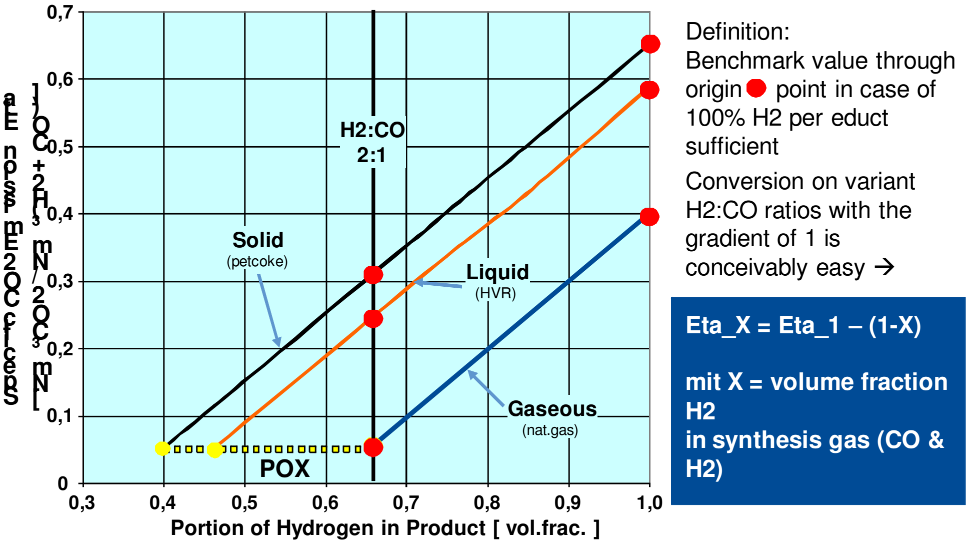


Figure 13 Specific emissions against the portion of hydrogen for several plants and different feedstocks (BASF 2009a)

Figure 13 shows the specific emissions against the portion of hydrogen in the syngas for several plants (red dots) and different feedstocks (gaseous - natural gas, liquid - high value residues (HVC), solid - petcoke). Each of the four functions corresponds to certain points in the diagram. The first function (hydrogen production, gas feed) corresponds to the red point on the blue line with the hydrogen portion 1. The second function (hydrogen production, liquid feed) cannot be connected to any point of the diagram at the moment. Those two functions describe the hydrogen production via steam reforming with methane (function 1) and naphtha (function 2) as feedstock.

The third and fourth function is the so called “upgrading function”. This is based on upgrading of heavy fuel oil (or other low-grade oil) to syngas or hydrogen. Such residues are exclusively used in the partial oxidation process (POX). For this function the actual point in the diagram is not known. It is assumed that the function corresponds to the red point on the red line with the H_2:CO ratio 2:1.

A function accounting for petrol coke as feedstock should due to our principles in any case not be included in the CWT approach, neither in the refinery nor in the chemical sector.

A complicating factor regarding the number of hydrogen units to be distinguished in the CWT approach and subsequently also for the chemical industry is that the different functions relate also to different H_2:CO ratios. Since the H_2:CO ratio is determining the specific emissions of the unit, the CWT approach has to account for the different H_2:CO ratios. For this the upper diagram and an approach by BASF may be used: The gradient of the straight lines describes the shift reaction process and is the same for all feedstocks. The higher the share of hydrogen in the synthesis gas (x-axis) and the lower the hydrogen in the feedstock, the higher are the related specific CO_2 emissions for a certain CO/H_2 composition. BASF's proposal is to correct in the benchmark for the different CO/H_2 ratios in accordance with the above given graph.

Potentially, after such correction for the actual CO/H_2 ratio of the syngas produced in the CWT approach, a uniform approach (i.e. a single overall function) for all syngas and hydrogen production units might be possible. The assumed ratios, which formed the basis for determining the CWT factors in the current CWT approach, are not known and are currently also being discussed between SOLOMON and CONCAWE. It is recommended to CONCAWE, Europia, EIGA and CEFIC to further discuss the possibility of merging the four H_2 / Syngas functions in the CWT approach into a single uniform approach with the CO/H_2 ratio of the product as parameter in the benchmark function or otherwise into at maximum two separate ones: one for the upgrading of heavy residues (combining the third and fourth function) and one for the production based on natural gas (combining the first and second function). In any case, the final approach for refineries should also apply to hydrogen plants in the chemical industry.

The performance factor should be ambitious in order to make the approach an approximation of the 10% best performers. EIGA gives some arguments for the ambition of the CWT approach which can be found in the stakeholder comments (chapter 7.4).

7.2.2 Final proposal for products to be distinguished

The production of synthesis gas belongs to NACE code 20.11 and the PRODCOM number of hydrogen is 20.11.11.50. There is no single PRODCOM number for carbon monoxide (20.11.12.90 is inorganic oxygen compounds of non metals) or synthesis gas.

7.3 Benchmark values

7.3.1 Background and source of data

Due to the existence of synthesis gas / H_2 plants in different sectors being operated by different parties there are several representatives. The refinery sector is represented by

CONCAWE / Europia, the chemical sector by Cefic and the industrial gas producers by EIGA (European Industrial Gas Association). Whilst EIGA is coordinating the response to the issue on behalf of EIGA / Cefic, EIGA / Cefic are working with Europia and CONCAWE to create an effective common approach for benchmarking H_2 / syngas plants.

7.3.2 Final proposed benchmark values

For on purpose hydrogen plants not operated by refinery operators, the implicit benchmark for hydrogen in the CWT approach (i.e. CWT for hydrogen production combined with the benchmark for t CO_2 / CWT) can be used. Pending the outcome of the further discussions on merging the various hydrogen related units in the refineries to one overall approach for hydrogen and synthesis gas, the indicative benchmark for refineries of 30 kg CO_2 / CWT needs to be multiplied with the resulting CWT factor for the hydrogen unit to calculate the final benchmark.

According to EIGA, a value for the production of hydrogen of 11 t CO_2 / t hydrogen, net of co-product steam, appears to be consistent with experience. The current CWT factor for hydrogen from gaseous feed is 296 (see sector report for the refinery industry), resulting in a hydrogen benchmark of 8.9 t CO_2 / t hydrogen.

7.3.3 Possibility of other approaches

More than 80% of the hydrogen for chemicals in the EU is used to produce ammonia (70%) and methanol (12%) (roads2highcom 2007). Therefore it might be possible to benchmark methanol plants in accordance to ammonia plants, which are also exclude from the hydrogen benchmark, by relating the benchmark not to the produced H_2 but to the end product, what results in an own product specific benchmark for all methanol plants.

7.4 Stakeholder comments

The joint intention of Refining, Chemicals and Industrial Gases sectors is to avoid distorting competition for hydrogen production between the three sectors in as simple and practicable a way as possible.

1. *Average* performance data for hydrogen installations and (potentially by extension) for syngas installations will be extracted from the Concave proposal for refinery benchmarking. It is expected that data will be provided for *at least* two classes of hydrogen installation depending on whether fed with gaseous, light liquid or possibly heavy liquid or solid feedstock and for one class of syngas installation.
2. It is expected that these data will provide the basis for broadly applicable hydrogen and syngas benchmark(s). The “emissions performance challenge” required for the success of the ETS would be applied through acceptance by the chemicals and industrial gases sectors of the same “challenge” as is proposed to be applied to existing refineries and to new captive refinery hydrogen and syngas installations for which free EUAs may be requested from the New Entrants’ Reserve: namely the ratio of benchmark performance to average performance for the refinery population
3. The by-production of heat – generally in the form of steam - in hydrogen

installations will be treated separately and in a manner consistent with the broad approach taken for benchmarking heat production in the ETS. In other words, a hydrogen installation will be considered for the purposes of benchmarking to be a producer of hydrogen and, separately where appropriate, a generator of heat. A syngas installation will be considered for the purposes of benchmarking to be a producer of syngas and, separately where appropriate, a generator of heat. No correction will be made at the benchmark stage for:
   a. Carbon dioxide import / export
   b. Electricity consumption for oxygen requirement
   c. Different H2 / CO ratios produced
4. Such corrections are necessary and will be applied at the stage of allocation of EUAs in order to maintain equity of treatment.
   a. If possible, correction for the electricity consumption for oxygen requirements - where relevant - should be made *without* recourse to a comprehensive and exhaustive benchmarking process for *oxygen*.
   b. Adjustments for reduction / elevation of emissions at different CO/H2 ratios may be made either by stoichiometric calculation or by empirical methods based upon the performance of existing installations.
5. For the purpose of clarity, the perimeter of HyCO installations shall be presumed to:
   a. Exclude feedstock- and product compression
   b. Exclude equipment for the purification of carbon monoxide from syngas
   c. Exclude electricity generation
6. Include PSAs, methanators etc. integrated with syngas generation

Regarding the ambition of the CWT approach compared to plant by plant benchmarking, it would require an extensive and confidential benchmarking exercise managed by a 3rd party to demonstrate that the approach proposed – including refinery-derived PCE and "emissions performance challenge" - would result in no lesser incentive to reduce greenhouse gas emissions than the extensive benchmarking exercise itself. However, EIGA & Cefic propose the following arguments to support the case that the refinery-derived approach would result in a powerful incentive to reduce emissions from hydrogen plants:

- The population of plants upon which the "CWT" for hydrogen plants is based under the CONCAWE / Solomon approach includes many large plants built in recent years by refineries to serve their captive requirements. These plants have been designed to meet modern efficiency standards
- The "emissions performance challenge" calculated for refineries as a whole will be strongly influenced by the characteristics of production units – "functions" - whose associated greenhouse gas emissions are predominantly combustion-related. In contrast, approximately one half of the greenhouse gas emissions from hydrogen plants results from unavoidable "stoichiometric" emissions from the shift reaction as shown in section 1.1 above – and a further proportion is unavoidable as a result of the endothermic character of the steam-methane reforming reaction. This produces the effect that the "emissions performance challenge" defined for refineries will, under the approach proposed by the consortium, be *calculated* on the *total* emissions from individual hydrogen installations but be achievable only through action focused towards the proportion of the emissions that is *avoidable* in those installations. The consortium recognizes that this effect will result in an

approximate doubling of the severity of the refineries' "emissions performance challenge" when applied to individual hydrogen plants.

7.5 Additional steps required

In order to use the CWT approach also for the chemical sector, it has to be further developed and verified, also in close relation to the work going on in the refineries sector.

8 Soda ash and sodium bicarbonate

More than 50% of the worldwide production of soda ash (sodium carbonate) is used to produce glass. Container and flat glass is made by melting a mixture of sodium carbonate, calcium carbonate and silica sand (SiO_2). To provide a good mixture, dense soda ash is used in the glass industry.

There are in total 16 plants and 5 companies in Europe producing sodium carbonate (3 in Germany, 2 each in UK, France, Poland, Romania and 1 each in the Netherlands, Italy, Spain, Portugal, Bulgaria). A plant in Austria (Ebensee) was closed in 2005.

8.1 Production process

The Solvay process for the production of soda ash may be summarized by the theoretical global equation involving the two main components sodium chloride and calcium carbonate.

$2\ NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$ (overall theoretical equation)

Equation 12

In practice this direct way is not possible and it needs the participation of other substances and many different process steps to get the final product soda ash.

The first reactions occur in the salt solution (brine). In a first step ammonia is absorbed (1) before then, the ammoniated brine is reacted with carbon dioxide to form successive the intermediate compounds ammonium carbonate (2) and then ammonium bicarbonate (3). By continuing the carbon dioxide injection and cooling the solution, precipitation of sodium bicarbonate is achieved and ammonium chloride is formed (4). The chemical reactions relative to the different process steps are given below:

(1) $NaCl + H2O + NH3 \rightarrow NaCl + NH4OH$ Equation 13

(2) $2\ NH4OH + CO2 \rightarrow (NH4)2CO3 + H2O$ Equation 14

(3) $(NH4)\ 2CO3 + CO2 + H2O \rightarrow 2\ NH4HCO3$ Equation 15

(4) $2\ NH4HCO3 + 2\ NaCl \rightarrow 2\ NaHCO3 + 2\ NH4Cl$ Equation 16

Sodium bicarbonate crystals are separated from the mother liquor by filtration, then sodium bicarbonate is decomposed thermally into sodium carbonate, water and carbon dioxide (5).

(5) $2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

Equation 17

CO_2 is recovered in the carbonation step (see equations 2 and 3 above). The CO_2 recovery cycle is shown in Figure 14.

The mother liquor is treated to recover ammonia. The ammonium chloride filtrate (4) is reacted with alkali, generally milk of lime (6), followed by steam stripping to recover free gaseous ammonia:

(6) $2\ NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2\ NH_3 + 2\ H_2O$

Equation 18

NH_3 is recycled to the absorption step (equation 1 above). The ammonia recovery cycle is shown in Figure 14.
Carbon dioxide and calcium hydroxide originate from limestone calcination (7) followed by calcium oxide hydration (8).

(7) $CaCO_3 \rightarrow CaO + CO_2$ Equation 19
(8) $CaO + H_2O \rightarrow Ca(OH)_2$ Equation 20

Brine (NaCl) has to be treated before being input into the process to remove impurities like calcium and magnesium. If such impurities were not removed, they would react with alkali and carbon dioxide to produce insoluble salts contributing to scale formation inside the equipment. Brine purification reactions are described with the following equations:

(9) $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ Equation 21
(10) $Mg^{2+} + 2\ OH^- \rightarrow Mg(OH)_2$ Equation 22

The chemical reactions previously described are realized industrially in the different process steps (plant areas) as illustrated in Figure 14:

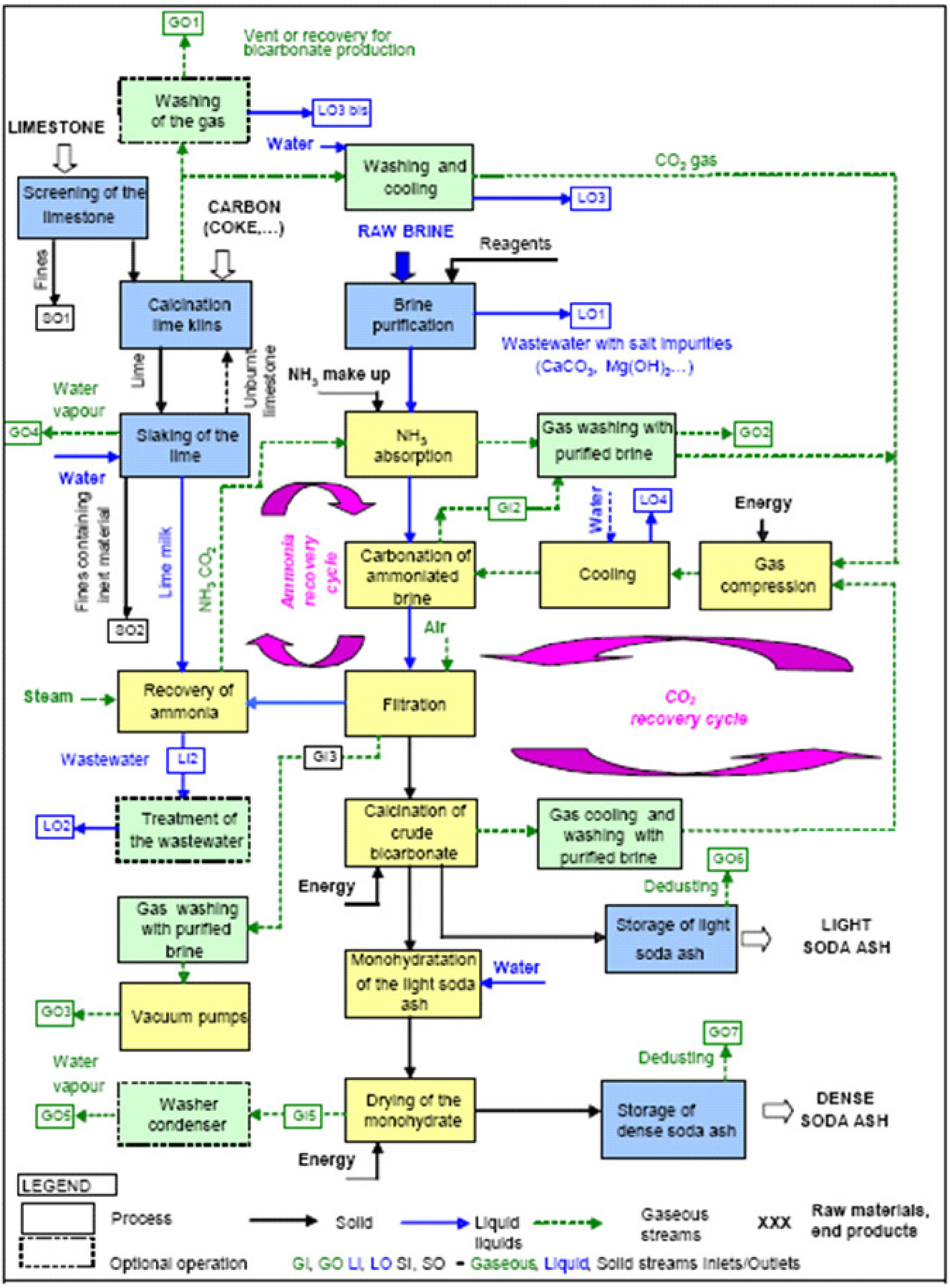


Figure 14 Process flow diagram for the manufacture of soda ash by the Solvay process (BREF – LVIC, 2007)

The limestone quality and availability differs from plant to plant. The $CaCO_3$ content varies in the range of 84 to 99%, which has a large impact on the energy consumption, because all raw limestone is burnt to CaO (BREF – LVIC, 2007).

8.2 Benchmarking methodology

8.2.1 Background

The European Soda Ash Producers Association (ESAPA) carried out benchmark analysis in cooperation with Cefic.

Approximately 12 out of 16 soda-ash plants have an integrated downstream sodium bicarbonate production unit ($NaHCO_3$). These plants generate less CO_2 emission since the CO_2 being produced in the soda ash plants is used as feedstock for the production of bicarbonate (as according to the reference document on BAT (BREF) on average 550 kg 100% CO_2 is used for the production of one t of $NaHCO_3$, whereof 260 kg CO_2 is captured by the product and 290 kg CO_2 is released to the atmosphere):

$$2\ Na_2CO_3 + CO_2 + H_2O \rightarrow 2\ NaHCO_3$$

Equation 23

ESAPA proposes to benchmark both the soda ash and the sodium bicarbonate production separately and argues, that sodium bicarbonate is explicitly mentioned in Annex I to the amended Directive and that operators of sodium bicarbonate plants should be rewarded for their investments and for using CO_2 as educt. The production of sodium bicarbonate consumes CO_2 and would therefore result in a negative benchmark. Plant operators would receive free allowances in the amount of this negative benchmark.

The consortium does not agree with ESAPA to reward sodium bicarbonate producers with free allowances. Amongst others sodium bicarbonate is used in the food industry to produce baking powder or in the pharmaceutical industry. In the baking process sodium bicarbonate is converted to H_2O and CO_2. CO_2 is therefore only temporarily stored and released to the atmosphere afterwards. The same applies for the taking of any pharmaceutical products; the CO_2 is not permanently stored. Regarding the aspect of sustainability it would not be justified to reward sodium bicarbonate producers with free allowances for the temporary storing of CO_2. Furthermore only the mention of sodium bicarbonate in the Annex I to the amended Directive does not imply that such installations are to be benchmarked, in particular if no GHG emissions are released by the production. The mention of sodium bicarbonate in the amended Directive only means that the production has to be accounted for in the EU ETS.

Unlike ESAPA we propose to deal with the soda ash / sodium bicarbonate production in the same way as with the ammonia / urea production (other downstream utilization using CO_2 as feedstock; see also chapter 5.2.1):

The benchmark accounts for all steam and process carbon dioxide emissions emerging exclusively from the soda ash production. The actual number of allowances for soda ash installations results from this benchmark value multiplied with the historical production of soda ash. The average carbon dioxide amount of a particular historical time period which was used as feedstock for a downstream sodium bicarbonate production is subtracted from the actual number of allowances for the soda ash installations. This subtraction happens ex ante, before the allowances are allocated. In this way the sodium bicarbonate production is included in the EU ETS and soda ash installations without a downstream bicarbonate production are not disadvantaged.

With this proposal the production of sodium bicarbonate is neither advantaged nor disadvantaged. Rewarding operators of sodium bicarbonate plants for their investments is not task of the EU ETS.

According to the principles, we oppose ESAPA's proposal to use an average emission factor for the whole soda ash production since this is a kind of correction for different feedstocks. The incentives should be the same for all plants operators (both within a certain industry and within the whole chemical sector) to invest in the most environmentally friendly technique.

8.2.2 Final proposal for products to be distinguished

The production of soda ash / sodium bicarbonate belongs to NACE code 20.13 and the PRODCOM numbers of the products are the following:

- Soda ash (density < 700 kg/m^3): 20.13.33.103
- Soda ash (density > 700 kg/m^3): 20.13.33.109
- Sodium bicarbonate: 20.13.43.20

The reference product is 1 t of soda ash.

8.3 Benchmark values

8.3.1 Background and source of data

The European Soda Ash Producers Association (ESAPA) carried out benchmark studies for the years 2005 and the period 2006-2007. Data for 2005 have been forwarded to the consortium.

8.3.2 Final proposed benchmark values

Due to a preparatory work for the reference document on best available techniques (BREF – LVIC, 2007), energy benchmarks have already been identified and used by ESAPA. Carbon dioxide emission (direct and from steam raising) and energy consumption benchmarking curves are therefore available.

Going from energy consumption benchmarks to carbon dioxide benchmarks, large differences between coal and gas based plants are visible (see Figure 15 below). While the most emission intensive plant has a specific emission factor of almost 2 t CO_2 / t soda ash, the most emission efficient plant emits only about 0.7 t CO_2 / t soda ash (2/3 off). This big difference results from the different feedstock use (energy carrier gas, fluid oils and coal). Plants using coal as feedstock are more emission intensive and therefore positioned at the right hand side in the benchmark curve, whereas plants being fed with gas are on the left hand side in the curve (t/t means t of CO_2 / t of soda ash):

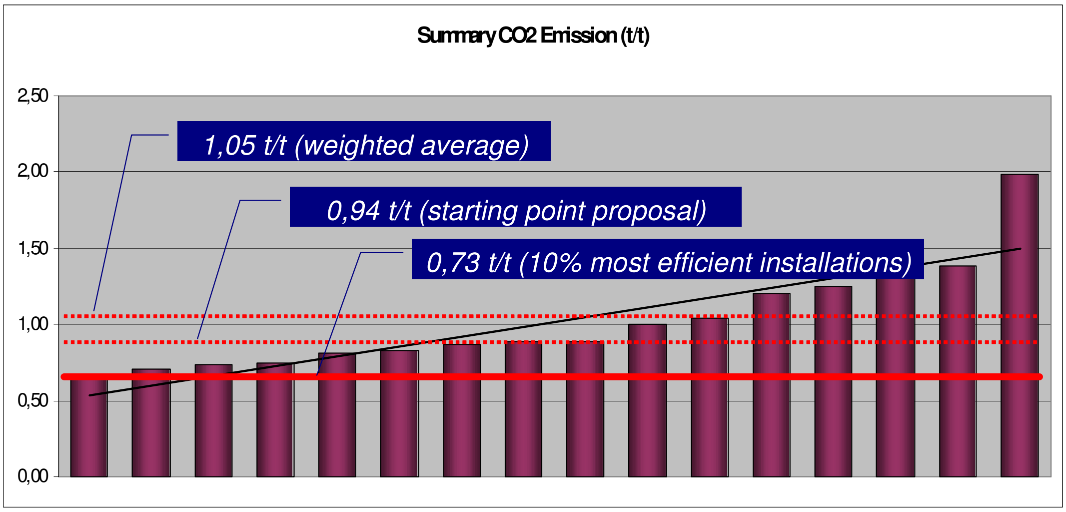


Figure 15 Emission benchmark curve for soda ash plants for 2005 (ESAPA 2009)

According to the benchmark study from <u>2005</u> the average best 10% benchmark is 0.73 t CO_2 / t soda ash.

8.3.3 Possibility of other approaches

There are two different approaches as described in chapter 8.2.1. ESAPA proposes to develop an own negative benchmark for the production of sodium carbonate whereas the consortium opposes this proposal and favours to deal with sodium carbonate in the same way as with ammonia / urea (other downstream utilization using CO_2 as feedstock).

8.4 Stakeholder comments

As announced previously ESAPA performed the benchmark exercise regarding 2006 and 2007. Results from 2005 have been already shared with you. Data for the period 2005 to 2007 are now therefore available.

ESAPA's main concern is the slope of the total CO_2 emission curve which is creating a huge different between sector average and benchmark (average of the best 10%). Taking into account the weighted average of 1.05 t / t soda ash implies that in average the soda ash production has to perform 36% better to reach the best plant (or 30% to reach the benchmark of 0.73 for the 10% most efficient installations). Obviously even worse and no sustainable when we are progressing from left to the right side of the curve, seeing the co-participation of other fuels (not natural gas) in the steam production.

Looking to energy efficiency and not to the impact of different emission factors and using the model Ecofys "fuel mix" presented in February 2009 Soda Ash has been proposing the solution:

BM Soda ash = Energy consumption benchmark x average emission factor + process emission benchmark.

Protect actual fuels portfolio seems prudent by security and strategic reasons (security purchasing decisions at industrial and national level). Shift to 100% natural gas in a context outlook 2013/2020 seems also by different reasons unrealistic.

About Sodium Bicarbonate the ESAPA proposal is: Installations should receive an additional amount of free allowances according the level of the benchmark that will be defined or in other words the amount of free allowances according the real positive impact in terms of CO_2 reduction. That position as explained could therefore protects the investment made by the integrated sites and naturally becomes an additional ex-ante product benchmark for the Sodium Bicarbonate activity also stipulated in Annex I to the amended Directive.

8.5 Additional steps required

The data should be updated with the inquiry for 2007/2008.

9 Aromatics

9.1 Production process

The following process description is extracted from an APPE paper (CEFIC 2009f):

Benzene, Toluene and Xylenes (ortho, meta and para) are the basic aromatics intermediates used for the manufacture of other chemicals (BTX). Figure 16 shows the schematics of the sources of feeds for the production of these three main aromatics as well as its main uses.

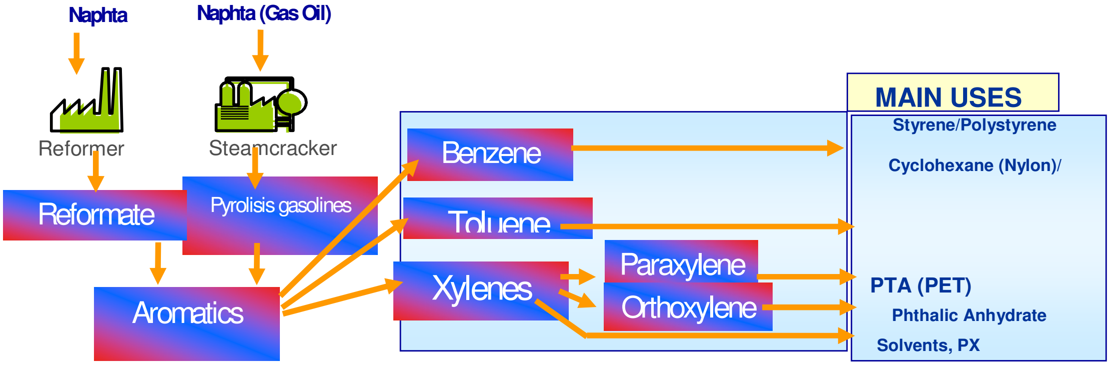


Figure 16 Sources of feeds for the production of benzene, toluene and xylene as well as its main uses (CEFIC 2009f)

As can be seen there are two main sources of feedstocks for the production of aromatics: pyrolisis gasoline produced in naphtha or gasoil steam crackers, and reformate from reformers. Reformers are typically found in refineries, so refineries produce a significant proportion of the overall aromatics production. Particularly xylenes are more conveniently produced from reformers than from pygas due to the higher yields that are obtained with this type of processes. A third industrial source of aromatics is coming from coke oven operations, which represents only a minor fraction of the aromatics production and its operation is not typically associated to conventional petrochemical industries.

The source of feedstock has an important impact on the process used for extraction of aromatics. In this sense we can distinguish four main process schemes for recovering aromatics based on the type of feed and product desired:

- Benzene and / or toluene extraction from pygas
- Benzene and / or toluene extraction from reformate
- Mixed xylenes produced from reformate
- Para-xylene and / or Ortho-Xylene extraction & isomerization from reformate (mixed xylenes)

Within these four main options there may be a lot of variations in the process scheme to accommodate to the particularities of each case; however the following description gives a generic indication of the required process.

Benzene and / or Toluene Extraction from Pygas

Raw pygas produced by steam crackers contains a large quantity of diolefins and olefins that need to be hydrogenate before extracting the aromatics. Also some other impurities such as sulphur need to be removed to obtain the specifications required in the aromatics. These requirements as well as the need to fractionate by distillation the desired cut (C6 cut for benzene and / or C7 cut for Toluene) determine the required process scheme, which in general will contain the following stages:

- A first stage hydrogenation of pygas for the conversion of diolefins and other very reactive species in olefins or other more stable compounds. This is done in a catalytic reactor at temperatures below 200°C and under a hydrogen pressure typically between 20-50 bars.
- A series of distillation operations to prepare the desired cut for the extraction. These distillation operations may include depentanizers, dehexanizers, deheptanizers, deoctanizers and rerun columns according to the particular scheme.
- A second stage hydrogenation to convert olefins in saturated species as well as to transform sulphur species in H2S that is further stripped in a column associated to the catalytic reactor. This reactor is operated at temperatures between 240°C and 350°C and at pressures typically below 50 bars. Some additional distillation may be required before extraction in some cases to removed heavies formed in the reactor.
- Aromatics extraction using either liquid-liquid extraction technologies or extractive distillation technologies. In both cases a solvent is needed to facilitate the separation of the aromatics from other species with very close boiling points, which prevents the use of conventional distillation. Most common solvents used are sulfolane, n-methyl-pyrrolidone (NMP), n-formyl-morpholyne (NFM) dimethyl-sulfoxyde (DMSO) or variations of molecules similar to sulfolane.
- Final distillations of the extracted aromatics when benzene and toluene (or even some xylenes) are extracted together to separate each aromatics species.

Benzene and / or Toluene Extraction from Reformate

Reformate products contain much lower quantities of olefins than pygas with no sulphur impurities so hydrogenation is not required. In this case the following steps are typically used:

- Fractionation of reformate by distillation to produce the desired cut for extraction.
- Extraction of aromatics in the same fashion as described in the case of pygas.
- Clay treating to remove traces of olefins in the extracted product. This is typically done heating the product at about 200°C in the presence of specific clays.
- Distillation of extracted aromatics when various species are extracted together

In some cases aromatics can be extracted jointly from reformate and pygas, which obliges to use a combination of both sequences of processes, previously described.

Mixed Xylenes from Reformate

A mixture of the three xylenes can be produced in some sites to be used either as solvents or as feed for further PX or OX extraction elsewhere. In this case the required steps are:

- Fractionation of reformate to produce the C8 cut rich in xylenes. This typically involves a deheptanizer column and another column to remove heavier molecules than the C8s.
- Clay treater to remove traces of olefins.
- When the reformate is coming from a reformer operating at low severity, it may contain significant quantities of non-aromatics C8 species that may require solvent extraction as described in the previous sections.

Para-Xylene and / or Ortho-Xylene from reformate

PX and / or OX are normally diluted in reformate C8 streams to about 20% each, being the meta-Xylene the most concentrated compound also with important amounts of ethyl-benzene. So the process is designed to convert as much as possible of the MX to PX / OX (when both products are desired) or MX / OX to PX when only this last one is the desired product. For doing so it is necessary a sequence of processes that are usually comprised within the so-called xylenes loop as follows:

- The C8 reformate cut is processed in a first column (xylenes column) where a purified C8 cut is obtained in the top. This distillation column is a very severe distillation that requires a lot of energy, which usually is heat-integrated with other units of the aromatics complex. When OX is also produced, the OX is separated in the bottom of the xylenes column with the C9 and heavies. In this case the column is even bigger and is usually referred as a super-fractionation unit.
- The C8 cut from the xylenes column is then processed in a special unit for recovering pure PX. C8 aromatic isomers have very close boiling points and chemical properties, so the separation of PX from other C8 aromatics needs to use other techniques. Two type of technologies are used for separating PX from the other C8 isomers:
    - o Shape selective adsorption of PX in a simulated moving bed adsorber taking benefit of the particular physical shape of this molecule
    - o Crystallization of the PX molecule at temperatures between –4 to –60°C, taking advantage of the higher melting point of the PX in relation to other isomers.
- The remaining C8 aromatics isomers after extraction of PX are sent to a xylenes isomerization unit where some more PX is produced from MX and OX. In this unit also the ethyl-benzene is dealkylated producing benzene that is recovered in a deheptanizer column and exported out of the xylenes loop. The isomerized C8 are recycled back to the xylenes column where they are mixed with the C8 reformate feed. Light decomposition products (mainly ethane) from the isom section are extracted as Isom gas which is mainly used to fire furnaces within the Px / Ox unit.

Additional processes : HDA and TDP

In some aromatics complexes there may be some additional processes for inter-conversion of aromatics molecules, especially from toluene, which is typically a less desired product, or from C9 aromatic molecules to obtain the most interesting benzene and xylenes products. The main processes used for that purpose are:

- Toluene Disproportionation (TDP) that takes place in presence of a catalyst to yield additional benzene an xylenes that are recovered somewhere else in distillation columns
- Selective Toluene Disproportionation (STDP) similar to the previous process but a shape selective catalyst allows to produce preferentially PX instead of the other isomers
- Toluene / C9 Aromatics transalkylation to produce also benzene and xylenes but in this case putting in the feed to this process also heavier aromatics as C9 or even C10s.
- Hydro-dealkylation (HDA) of Toluene and / or Xylenes to yield benzene. Thermal process that removes alkyl groups from the aromatic ring.

9.2 Benchmarking methodology

9.2.1 Background

Aromatics are produced both in the chemical and the refinery sector. Aromatics units situated in refineries are currently part of the refinery benchmark (CWT approach). Cefic and PTAI (Philip Townsend Associates Inc., consultant for the petrochemical industry) indicated two different possibilities how to cover aromatics plants in the chemical sector:

1. Individual production benchmark for aromatics production within the chemical sector
   Develop criteria which define unambiguously whether an aromatics unit is a refinery type or petrochemical type. In this option, PTAI benchmark would be based on 2007-2008 data for petrochemical-type aromatics units only. The refinery benchmark would be applied to refinery-type aromatics units and the PTAI benchmark to petrochemical aromatics units. However, the current data base of PTAI contains both petrochemical and refinery type aromatics units. There is thus a risk that PTAI and refinery benchmark would result in different CO_2 allocations for an aromatics unit.

2. CWT approach
   Use the same CO_2 allocation factors for petrochemical aromatics units as for the refinery benchmark. This would be similar to the methodology currently considered for H_2 production plants and would have the big advantage of preventing aromatics operators trying to position themselves either as petrochemical or refinery type to maximise allocations (this applies especially for those aromatics units that take feed both from a cracker and a reformer and thus may be difficult to clearly allocate to a refinery or petrochemical unit). The refinery benchmark is however based on crude throughput and expresses the benchmark based on “complexity weighted t” (CWT). The concept of CWT compares the CO_2 intensity of the various units in the refinery to that of the crude distiller. As a petrochemical aromatics unit is not necessarily linked to a crude distiller on the site, Cefic does not know whether the refinery methodology could be applied to aromatics units on a petrochemical complex. This subject is under discussion between Cefic and EUROPIA (European Petroleum Industry Association) / CONCAWE (The oil

companies' European association for environment, health and safety in refining and distribution) and Cefic will explore in the coming months if the concept of CWT restricted to aromatics units could form an alternative to possibility 1.

We propose to use the CWT approach (possibility 2) which was developed by CONCAWE, the representative of the refinery sector and which includes implicit benchmarks for aromatics production units. This ensures that there will not be any distortions between the chemical and the refinery sector due to unequal treatment of both sectors.
For the first possibility Cefic proposes two methods how to develop own production benchmarks for aromatic units in the chemical sector. Those approaches can be found in the chapter 9.3.3 (possibilities of other approaches).

The CWT approach includes the following functions to describe the aromatics production (and derivatives):

- Aromatic Solvent Extraction
- Hydro dealkylation (toluene)
- Thiamine diphosphate (TDP) / Toluene diisocyanate (TDA)
- Cyclohexane
- Xylene Isomerization
- Para-xylene
- Ethyl benzene
- Cumene

At this point we refer to the sector report for the refineries and chapter 7 (hydrogen and syngas), where the CWT approach is explained in detail.

9.2.2 Final proposal for products to be distinguished

The production of aromatics belongs to NACE code 20.14. Using the CWT approach several products can be derived from the above CWT functions. The PRODCOM numbers of those products are the following:

- Aromatic Solvent Extraction → Benzene: 20.14.12.23
- Aromatic Solvent Extraction / Hydro dealkylation → Toluene: 20.14.12.25
- Aromatic Solvent Extraction → Ortho-xylene: 20.14.12.43
- Aromatic Solvent Extraction → Meta-xylene: 20.14.12.47
- Xylene Isomerization → Isomeric xylene: 20.14.12.47
- Para-xylene: 20.14.12.45
- Thiamine diphosphate: 20.14.53.50
- Toluene diisocyanate: 20.14.44.50
- Cyclohexane: 20.14.12.13
- Ethyl benzene: 20.14.12.60
- Cumene: 20.14.12.70

It is mentioned that for the CWT process functions “Aromatic Solvent Extraction” and “Hydro dealkylation” the benchmark is not related to a certain product, but to the whole process unit. In those units several products are produced (e.g. benzene, toluene, xylene). That means that the benchmark is related to the product mix (similar to the HVC at steam cracking).
For the other process functions it is assumed that the benchmark can be related to the corresponding product (e.g. the benchmark for the function “cyclohexane” to the product “cyclohexane”). However, this needs to be further investigated.

9.3 Benchmark values

9.3.1 Background and source of data

Since we propose to use the CWT approach developed by CONCAWE also for aromatics produced in the petrochemical sector, the CWT factors for the various aromatics units in refineries and the benchmark for the CO_2 weighted t (final benchmark not yet available, see sector report for the refineries) are required to determine the allocation for aromatics production. Multiplying both values results in the final process related benchmark.

9.3.2 Final proposed benchmark values

The CWT factors for the several aromatics process units are (see also chapter 3.2 of the sector report for the refineries):

Aromatic Solvent Extraction	5.25
Hydrodealkylation	2.45
TDP/TDA	1.85
Cyclohexane	3.00
Xylene Isom	1.85
Paraxylene	6.40
Ethylbenzene	1.55
Cumene	5.00

The indicative CWT benchmark level is 30 kg CO_2 / CWT (see also chapter 7 of the report on the project approach and general issues and chapter 4 of the sector report for the refineries). Multiplying the CWT factors with the CWT benchmark level, results in the benchmark level for the corresponding process unit / product.

9.3.3 Possibility of other approaches

PTAI is one of the leading consultants on benchmarking in the petrochemical industry and has in the past carried out benchmarks for aromatics complexes.

PTAI has developed a benchmark methodology for a generic aromatic complex (i.e. covering both refinery type and petrochemical type aromatics units). The generic aromatics complex is divided into 6 unit blocks (the reformer is excluded from petrochemicals benchmark), as shown schematically in Appendix 1.

Cefic has approached PTAI to generate a benchmark for aromatics units. This will be done in two phases. First, PTAI will use its actual database of aromatics plants to evaluate and identify suitable benchmarks. Further, Cefic plans to launch a second phase with PTAI to collect the required data for the years 2007-2008 for all "appropriate" aromatics plants in Europe to allow to calculate the CO_2 benchmark according to the method(s) retained. Planning is to start this data collection phase in September 2009 and to have benchmark data available by the end of the year. If by September, no decision has yet been made on the preferred methodology to calculate the benchmark, sufficient data will be collected to be able to calculate the benchmark according to the various methodologies still under discussion.

Cefic and PTAI judge that one simple benchmark may present too much of a simplification to cover all aromatics units in a fair way because of difference in complexity of various aromatics units depending on the products made (some producing only benzene, others producing all BTX including paraxylene as a separate product). Currently, Cefic and PTAI have identified two approaches.

Method One:
Pygas with hydrotreating to feed BTX extraction, with results given in t CO_2 / t BTX extracted

- Reformate feed to BTX extraction without hydrotreating, results given in t CO_2 / t BTX extracted
- Paraxylene and orthoxylene extraction, results given in t CO_2 / t xylenes

Method Two:

- Pygas, results given in t CO_2 / t feed
- BTX, results given in t CO_2 / t BTX extracted
- Paraxylene and orthoxylene extraction, results given in CO_2 t / t xylenes (same as in Method One)

PTAI has used data from the previous benchmark exercise in 2006 to generate typical emissions intensity factors for each of the two methods. Some preliminary results are shown below. Cefic and PTAI are currently reviewing the merits and problems of each method. PTAI is also considering how to include corrections for those aromatics units that operate HDA or TDP plants.

Results of the evaluation:
In the 2006 data, no data were collected on the composition of the fuel burned in furnaces, only energy consumption in these furnaces was considered. Data on steam consumption, electricity consumption and heat integration were however collected. The various energy vectors were converted to CO_2 using the following factors.
Fossil fuel conversion factor = 0.08 t CO_2 / GJ LHV
Steam conversion factor = 0.072 t CO_2 / GJ steam (or heat)
Electricity conversion factor = 0.7 t CO_2 / MWh.

Table 12 Method 1 (Industry average)

Benchmarked section	Basis	Region	Direct+heat (t CO_2/t)	Direct+heat+electricity (t CO_2/t)
Pygas+BTX from raw pygas	BTX production	Europe	0.38	0.43
BTX of reformate	BTX production	World	0.26	0.28
Xylenes loop	P+O-xylenes	Europe	0.50	0.65

Table 13 Method 2 (Industry average)

Benchmarked section	Basis	Region	Direct+heat (t CO_2/t)	Direct+heat+electricity (t CO_2/t)
Pygas	Feed	Europe	0.08	0.10
BTX extraction	BTX produced	Europe	0.26	0.27
HDA	BTX produced	World	0.32	0.40
TDP	BTX produced	World	0.34	0.38
Xylenes loop	P+O-xylenes	Europe	0.50	0.65

Remark: in method 2, PTAI has also considered the impact of HDA and TDP processes on the emissions. There are only a few HDA and TDP units in operation within European petrochemical aromatics units, benchmark of these units separately using only European data will not be possible. Cefic and PTAI are looking at best way for correcting CO_2 allocations for the few petrochemical aromatics units in Europe operating TPD or HDA.

9.4 Stakeholder comments

Remark on Cyclohexane:
Cyclohexane is made by hydrogenating benzene. This is an exothermic process and has no direct furnace emissions and very low steam related emissions. It is proposed to exclude cyclohexane from the benchmarking process of aromatics and deal with cyclohexane production as one of the left over products.

Remark on benzene from coke ovens:
A small fraction of benzene is also produced from coke ovens. Given that this represents only a minor fraction of all aromatics produced, given that coke oven processes are very different and given that they are not covered in the usual benchmarking exercises by PTAI (nor Solomon), Cefic recommends that these processes are treated in the same way as the left over products.

9.5 Additional steps required

It has to be further investigated in what way the CWT approach of the refinery sector may need to be adapted / refined to include also additional aromatics units in the chemical sector.

10 Carbon black

10.1 Production process

Today there are 23 carbon black installations in the EU27. However, the total number of plants decreases. The plants in Berre L'etang (F), Stanlow / Ellesmere and Avonmouth (both UK) will be closed. In addition the Belgian plant does not fulfil the minimum energy criteria and is therefore not included in the EU ETS. As a result there are 19 carbon black installations covered by the EU ETS belonging to the companies Columbian, Evonik and Cabot.

Table 14 Locations and number of carbon black plants (BREF - LVIC, 2007)

Country	Capacity (kt / year)	Number of plants	Location
Germany	365	3	Dortmund, Hannover, Hürth-Kalscheuren
France	305	3	Berre L'etang, Lillebonne, Ambes
Italy	245	3	Ravenna, Ravenna, S. Martino di Trecate
United Kingdom	210	2	Stanlow / Ellesmere, Avonmouth
Netherlands	155	2	Rozenburg, Botlek-Rotterdam
Spain	120	2	Puerto de Zierbenna, Santander
Sweden	40	1	Malmö
Belgium	10	1	Willebroek
Portugal	35	1	Sines
Czech Republic	75	1	Valasske-Mezirici
Hungary	70	1	Tiszaujvaros
Poland	45	2	Jaslo, Gliwice
Total EU-25	**1675**	**22**	
Romania	30	1	Pitesti
Croatia	40	1	Kutina
Total Europe	**1745**	**24**	

More than 2/3 of the total carbon black production goes to the tire industry. The other 1/3 is used to produce mechanical rubbers, plastics, inks and colours. The use of carbon black for such different applications requires different grades which are defined by e.g. the particle size or the carbon content.

In Europe there are three different processes to produce carbon black:

- Furnace Black process
- Gas black process
- Lamp back process

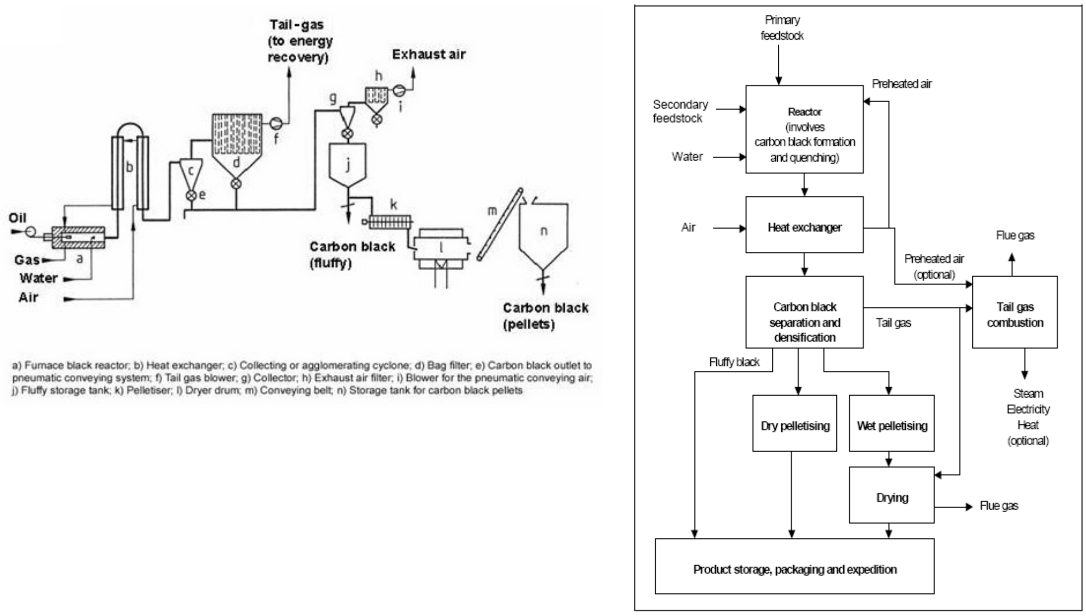
The following table gives the worldwide share of the individual processes in the total production:

Table 15 Manufacturing processes and feedstock used for the production of carbon black (ICBA 2009)

Chemical process	Manufacturing process	Percentage of global production	Feedstock
Partial combustion	Furnace black process	>95%	Petrochemical oils, coal tar oils and natural gas
	Gas black process	< 5%	Coal tar oils
	Channel black process		Natural gas
	Lamp black process		Petrochemical / coal tar oils
Thermal cracking	Thermal black process		Natural gas, oil
	Acetylene black process	<5%	Acetylene

The furnace black process is the most common process. The use of the gas black or lamp black process accounts for less than 5% of the worldwide carbon black production. According to the European members of the ICBA (International Carbon Black Association) in Europe one plant is based on the gas black and one on the lamp black process within the EU ETS (both EVONIK).

The furnace black process is illustrated in the following schematic process flowsheet (left figure) and the basic flow chart (right figure).



a) Furnace black reactor; b) Heat exchanger; c) Collecting or agglomerating cyclone; d) Bag filter; e) Carbon black outlet to pneumatic conveying system; f) Tail gas blower; g) Collector; h) Exhaust air filter; i) Blower for the pneumatic conveying air; j) Fluffy storage tank; k) Pelletiser; l) Dryer drum; m) Conveying belt; n) Storage tank for carbon black pellets

Figure 17 Schematic process flowsheet (left) and example of possible configuration of the furnace black process (right) (ICBA2009)

The following process description is extracted from the reference document on best available techniques (BREF – LVIC, 2007):

"The heart of a furnace black plant is the furnace in which the carbon black is formed. The primary feedstock is injected, usually as an atomised spray, into a high temperature zone of high energy density, which is achieved by burning a secondary feedstock (natural gas or oil) with air. The oxygen, which is in excess with respect to the secondary feedstock, is not sufficient for complete combustion of the primary feedstock, the majority of which is, therefore, pyrolysed to form carbon black at 1200 – 1900 °C. The reaction mixture is then quenched with water and further cooled in heat exchangers, and the carbon black is collected from the tail-gas by a filter system.

The primary feedstock, preferably petrochemical or carbo-chemical heavy aromatic oils, some of which begin to crystallise near ambient temperature, is stored in open to air, vented and heated tanks equipped with circulation pumps to maintain a homogeneous mixture. The primary feedstock is pumped to the reactor via heated and / or insulated pipes to a heat exchanger, where it is heated to 150 - 250 °C to obtain a viscosity appropriate for atomisation. Various types of spraying devices are used to introduce the primary feedstock into the reaction zone.

The energy to break C-H bonds is supplied by feedstock, which provides the reaction temperature required for the specific grades. Natural gas, petrochemical oils and other gases, e.g. coke oven gas or vaporised liquid petroleum gas may be used as secondary feedstock. Depending on the type of secondary feedstock, special burners are also used to obtain fast and complete combustion. The required air is preheated in heat exchangers by the hot carbon black containing gases leaving the reactor. This saves energy and thus improves the carbon black yield. Preheated air temperatures of 500 – 700 ºC are common."

Parameters like temperature and degree of quenching can be changed to get different grades of carbon black. The yield of carbon black and thus energy consumption and specific carbon dioxide emissions can vary on a wide scope. The yield varies from 40%-65% for rubber blacks and from 10%-30% for high surface pigment blacks. However, the total direct CO_2 emissions for a given plant are rather similar year on year because of the mixture of grades produced at that site.

An important aspect in the carbon black production is the use of the tail gas. The tail gas consists of 30-50% water vapour, 30-50% nitrogen, 1-5% CO_2 and small amounts of CO and H_2. This low caloric mixture enables energy recovery by producing heat, steam or electricity. The following table shows the different uses of tail gas in European and American installations.

Table 16 Tail gas combustion control devices (ICBA2009)

Control device	Europe	US	Total
Boiler	10	3	13
Combined Heat and Power (CHP)	13	-	13
Flare	7	8	5
Thermal combustor	1	8	9
No control	1	3	4
Tail-gas sold	2	-	2
Not available (unknown)	4	2	6

Most installations produce steam, hot water or electricity for sale. The GHG emissions emerge exclusively from the (partial) combustion of fuel (primary and secondary feedstock) and occur when the tail gas is burnt.

10.2 Benchmarking methodology

10.2.1 Background

For benchmarking the process, we propose a methodology comparable to the one used for the waste gases in the iron and steel industry (described in the iron and steel sector report and chapter 6 of the report on the project approach and general issues). In this way, installations selling the tail gas or using it for the production of electricity and / or steam are positioned on the left hand side of the benchmark curve, whereas installations flaring the gas will occur on the right hand side of the curve[10], which is the desired result. In the allocation methodology for the tail gas consumer, the tail gas should be taken into account as if it was natural gas as well. If the tail gas is used for electricity production, no allowances will be given in principle but this also depends on the final political choice on this issue (see report on the project approach and general issues and the iron and steel sector report on this issue). If used for heat production under a combustion process benchmark, allowances based on this benchmark should be given to the consumer. As explained in the report on the project approach and general issues, we leave the discussion on the dynamic aspects related to this methodology (i.e. the actual use of the tail gas might change over time) outside the scope of this study.

According to the European members of the ICBA the gas black and lamp black plants should be excluded from the benchmarking. They argue that those plants produce special grades of carbon black which cannot be produced with the furnace black process.

The consortium proposes for the above reasons to exclude those plants from benchmarking. The different grades can be considered as different products what justifies an exclusion, because the specific emissions of both processes vary from those of the furnace black process; the emissions of the gas black process are up to 4 times higher than those of the furnace black process, those of the lamp black process are up to 70% lower. The yield of carbon black and therefore the emission intensity strongly depend on the produced quality. With the gas black process high quality pigment blacks with a small particle size are produced, whereas with the lamp black process – the oldest industrial scale production process – rather coarse blacks with a mean particle diameter of approximately 100 nm are produced. Those different product qualities explain the different emission intensities of the gas and lamp black process compared to the furnace black process.

In addition the emission share of those two installations in the total CO_2 emissions of all carbon black installations is very low. According to the CITL database the verified emissions of those two installations account for 58550 t CO_2. The share in the total emissions (4.6 Mt CO2, see Table 3 in chapter 2) results is only 1.27%.

---

[10] If only the CO_2 emissions as calculated by the carbon balance would be plotted, the installations would be positioned at the same position of the curve, regardless whether the tail gas is used or flared.

10.2.2 Final proposal for products to be distinguished

The PRODCOM code for carbon black is 20.13.11.30 and the NACE code for the sector is 20.13 (Manufacture of other inorganic basic chemicals). The reference product is 1 t of carbon black from the furnace process. It should be further discussed how the carbon black from the gas and lamp black processes (fall-back approach) can be clearly distinguished from the carbon black for which a benchmark approach is proposed, e.g. by the particle size of the produced carbon black.

10.3 Benchmark values

10.3.1 Background and source of data

The European members of the ICBA started working on benchmarking carbon black plants and developed a questionnaire to be filled in by the different plant operators. They are supported by a consultant and for reasons of confidentiality the collected data are amenable exclusive for a law office. The questionnaire demands inquires about input energies, products and emissions like

- General information and instructions
- General process and technical questions
- Input raw materials and energies (Y 2005-2007)
- Output Carbon Black, key physical data, grade related input data (Y 2005- 2007)
- Direct emissions (Y 2005-2007) calculated or validated; allocation (Y 2008 – 2012)

The data are currently examined by the consultant, so benchmarks are not available yet.

10.3.2 Final proposed benchmark values

The European members of ICBA claim that “due to anti-trust and competitiveness issues, detailed results cannot be given as this would allow detailed insights to the position of competitors’ plants along the CO_2 intensity curve.

Since the European members of the ICBA do not deliver any absolute figures concerning the emission intensity, the consortium is not able to determine a benchmark value.

To give an approximate value, we take the IPCC emission factor which is 2.62 t CO_2 / t CB. It should be noted, however, that in this emission estimate, all emissions from the tail gas are included without the subtraction for the emission factor of natural gas.

For carbon black produced by other processes than furnace black, we propose basing the allocation of allowances on a fall-back approach (see section 5 of the report on the project approach and general issues).

10.3.3 Possibility of other approaches

There are no reasons for other approaches.

10.4 Stakeholder comments

The ICBA does not agree on the natural gas deduction for the tail gas use on the producer side for deriving the benchmark level. They want to include all CO_2 emissions to be determined as described in chapter 10.2.1 at the producer side (carbon balance), however, without the deduction for the tail gas use. They argue that the consideration of the tail gas use at the benchmarking stage disadvantages non-integrated plants which do not have the opportunity to sell the tail gas or at which steam production is not profitable. In their approach a good plant efficiency would be rewarded, whereas in our approach the environmental friendly use of the tail gas is rewarded in addition. The ICBA want to account for the tail gas use only at the allocation stage.

10.5 Additional steps required

It is essential to deliver the benchmark curve in order to determine the final benchmark value. There are only 3 players on the European carbon black market and anti-trust and competitiveness issues thus play a particular important role. However, there are 17 installations to be benchmarked what makes it in our opinion impossible to assign a certain installation on the benchmark curve to a certain company, particularly if all installations in the curve are very close to each other. It is therefore strongly recommended to further discuss with the carbon black sector whether it is possible to disclose benchmark curves based on the data collection effort conducted by the industry.

11 Glyoxal and glyoxylic acid

Glyoxal is the smallest possible dialdehyde with the structure OHC-CHO. Oxidation of glyoxal generates glyoxylic acid (OHC-COOH). There are two production sites for glyoxal in the EU27: BASF, Ludwigshafen and Clariant, Lamotte. Only the latter facility uses a production process which releases N_2O. A third European producer of glyoxylic acid is DSM, but an explosion in 2003 at DSM's plant in Linz, Austria, forced the operator to cease the production. DSM used a new process with ozonolysis of maleic acid dimethyl ester and hydrolysis of the ozonides. It is unknown if and when the production will start again.

The application fields of glyoxal are very wide, see the following table:

Table 17 Different applications of glyoxal (BASF 2009a)

Application	Characteristic	Benefit
Textiles	Crosslinking agent or building block for crosslinker	Softer and less wrinkled textiles
Paper	Crosslinking agent or building block for crosslinker	Paper wet strength (e.g. toilet paper) Paper dry strength (e.g. recycled paper) Efficient paper coating additive for high-quality papers
Leather	Crosslinking in tanning process	Preservation of leather quality
Cosmetics	Use of glyoxal-crosslinking polymers (hydrocolloids)	Better viscosity
Epoxy	Building block for specific epoxy applications	Higher epoxy stability performance
Oil & Gas	Biocide Sulfur scavenger Use of glyoxal-crosslinking polymers (hydrocolloids)	Anti-corrosive Safety at work Improves viscosity in oil-drilling fluids
Disinfection	Biocidal active ingredient for disinfection formulations	Co-biocide for disinfectants used in the health industry and in veterinary hygiene Effective when formulated together with e.g. glutaraldehyde
Glyoxylic Acid	Raw material	Serves as an intermediate for vanillin, agricultural chemicals, antibiotics, allantoin, complexing agents
Wood Hardening	Crosslinking agent or building block for crosslinker	Cures wood Protection from moisture

Glyoxylic acid is used for special chemicals like scents, flavoring agents, agro chemicals, dyes, pigments and others.

The N_2O emissions from the glyoxal/glyoxylic acid production accounts for only 0.2% of the overall CO_2 emissions (CO_2-equivalents) from the chemical sector in the EU and is therefore not within the 80% most emission intensive activities (see `Table 3` in Chapter 2). As a result this activity would be covered with a fall-back approach (see section 5 of the report on the project approach and general issues). However, the glyoxal / glyoxylic acid production is mentioned explicitly in Annex I to the amended Directive and a different allocation method could be applied. That is why we include an own chapter for glyoxal and glyoxylic acid in this report.

11.1 Production process

The worldwide production volume of glyoxal is estimated to be approx. 120000 to 170000 t (OECD 2009). BASF is the largest producer with a world-scale production capacity of 80000 t (60000 t in Ludwigshafen, Germany, and 20000 t in Geismar, USA).

There are two possible routes for producing glyoxal and both are continuous processes. BASF produces Glyoxal by a gas phase oxidation of ethylene glycol in the presence of a silver or copper catalyst. This process only emits CO_2.

$$CH_2OH - CH_2OH + O_2 \xrightarrow{[Kat.]} 2\,CHOCHO + 2\,H_2O$$

Equation 24

The second process, liquid phase oxidation of acetaldehyde with nitric acid, emits CO_2 and N_2O and is used in Europe only at the Clariant´s Lamotte site in France since 1960 (see the following equation).

$$2\,CH_3CHO + 2\,HNO_3 \rightarrow 2\,CHOCHO + 3\,H_2O + N_2O$$

Equation 25

The stochiometric relationship indicates that a complete reaction will produce 380 kg N_2O / t of glyoxal, under process conditions there are 520 kg N_2O produced (ENTEC 2008, IPCC, 2006). A N_2O destruction rate of 80% is assumed. The following table shows the historical N_2O emissions of the Lamotte site (REP 2009):

Table 18 Total N_2O emissions emitted by the glyoxal plant in Lamotte

	2005	**2004**	**2003**
N_2O [kg/a]	1250000	1280000	1110000

The production capacity of the Lamotte site is not available. According to ENTEC (2008), Clariant uses a thermal treatment with a specific catalyst as abatement technology since 2001.

The processing of glyoxylic acid happens with a batch process where nitric acid is reduced to NO and N_2O with NO recovered as HNO_3 in the process. N_2O arises in the production process due to a secondary reaction where glyoxal is converted to glyoxalic acid $(COOH)_2$:

$$2\,CHOCHO + 2\,HNO_3 \rightarrow 2\,(COOH)_2 + N_2O + H_2O$$

Equation 26

The default factor for glyoxylic acid from the IPCC guidelines is 0.1 t N_2O / t product (0.02 t after abatement).

The productions of glyoxal, but also the production of glyoxylic acid, which takes place also at Lamotte, generate off-gas in varying quantities. Typical N_2O concentrations in the off-gases are > 90 % for glyoxal and approx. 12% for glyoxylic acid. The performance of a fresh catalyst is > 95%, but it decreases to ca. 80% after one year.

11.2 Benchmarking methodology

11.2.1 Background

There is only one production site in Europe where glyoxal and glyoxylic acid are produced in a process that emits N_2O. The remaining European sites do not generate any direct greenhouse gas emissions. Due to only one plant within the EU ETS, benchmarking is not feasible and thus a fallback approach should be applied. In order to provide for an incentive to reduce the N_2O emissions, as an alternative a technology specific BAT benchmark could be developed which corresponds to the BAT of the abatement technique.

11.2.2 Final proposal for products to be distinguished

The production of glyoxal and glyoxylic acid belongs to NACE code 20.14 and the PRODCOM number is 20.14.61.20 (cyclic aldehydes; without other oxygen function) for glyoxal and 20.14.34.75 (carboxylic acid with alcohol, phenol, aldehyde or ketone functions) for glyoxylic acid respectively. Since pure glyoxal is not stable in the natural atmosphere, it is traded in a 40% aqueous solution. Glyoxylic acid is a solid.

11.3 Benchmark values

11.3.1 Background and source of data

The consortium tried to contact the Lamotte site via Email but has not received any response so far. No data are available to Cefic as well.

11.3.2 Final proposed benchmark values

A technology specific benchmark based on the BAT of the abatement technique has not been developed yet.

11.4 Stakeholder comments

None

11.5 Additional steps required

For the production of glyoxal via the HNO_3 / N_2O route the important points seem to be known, but the actual data need to be provided by Clariant.

12 References

APPE (2009a), European Chemical Industry Council; Homepage: www.Cefic.be

APPE (2009b), Email communication with APPE on 24th July 2009

APPE (2009c),Presentation by APPE, at a meeting with Fraunhofer ISI on 19th June 2009: "Correction factor in the CO_2 benchmark"

APPE (2009d), Presentation by APPE, at a meeting with Fraunhofer ISI on 26th March 2009: "Petrochemicals Benchmark"

Arpe (2006), H.-J. Arpe; Industrial Organic Chemistry; Wiley-VCH; 2006

BASF (2009°), http://www.intermediates.basf.com/en/intermed/products/glyoxal/-application/application-glyoxal.htm.

BASF (2009b), Presentation by BASF at a meeting with Fraunhofer ISI on 21 April 2009: "Kohlendioxidemissionen bei der Herstellung von Synthesegas und Wasserstoff".

BREF - LVOC (2003), Integrated Pollution Prevention and Control (IPPC): Reference Document on Best Available Techniques in the Large Volume Organic Chemical Industry, February 2003

BREF – LVIC (2007), Integrated Pollution Prevention and Control (IPPC): Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals - Solids and Others industry; August 2007

BREF – Ammonia (2007), Integrated Pollution Prevention and Control (IPPC): Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilisers; August 2007

CEFIC (2009a), Cefic Proposal for an ETS Benchmark Methodology for Annex I Installations; 30th April 2009

CEFIC (2009b), Email communication with Cefic on 24th June 2009

CEFIC (2009c), Email communication with Cefic on 30th June 2009; Cefic comments on the Ecofys/Fraunhofer/Öko-Institut consultation papers: "Project approach and general issues concerning a free allocation methodology for the ETS post 2012" (19 May) & "First draft report for the chemical sector" (26 May 2009)

CEFIC (2009d), Meeting with Cefic on 23rd April 2009 in Brussels

CEFIC (2009e), Email communication with Cefic on 07th August 2009

CEFIC (2009f), Aromatics: Overview and basic considerations for a CO_2 Benchmark; Philip de Smedt, Cefic; 2009

Chemplan (2009), http//:www.chemplan.com/chemplan_demo/sample_reports/ Adipic_acid.pdf

ECHA (2008), European Chemicals Agency: LIST OF PRE-REGISTERED SUBSTANCES PUBLISHED. Press Release ECHA/PR/08/59. http://echa.europa.eu/doc/press /pr_08_59_ publication_pre-registered_substances_list_20081219.pdf Helsinki, 19th December 2008

EC (2008), European Commission Decision (C(2008) 7867) of 17.12.2008 concerning the unilateral inclusion of additional greenhouse gases and activities by the Netherlands in the Community emissions trading scheme pursuant to Article 24 of Directive 2003/87/EC of the European Parliament and of the Council

EEA (2009), European Energy Agency; National greenhouse gas inventories (IPCC Common Reporting Format sector classification); 2009

EFMA (2009a), Email communication with EFMA on 8th September 2009

EFMA (2009b), Email communication with EFMA on 30th June 2009

EFMA (2009c), Email communication with EFMA on 24th July 2009

EFMA (2009d), Email communication with EFMA on 26th March 2009

ENTEC (2008), ENTEC UK Limited: Support for the Development and Adoption of Monitoring and Reporting Guidelines and Harmonised Benchmarks for N_2O Activities for Unilateral Inclusion in the EU ETS for 2008-12. Final report; London; February 2008

ESAPA (2009), Presentation at Cefic in Brussels, 23rd of April 2009.

ICBA (2009), Presentation by the European members of the ICBA affected by the Emission Trading Scheme at meeting with Fraunhofer ISI on 6th May 2009

IPCC (2001), H. Mainhardt; N_2O emissions from adipic acid and nitric acid production; Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories, p.183; IPCC; 2001

IPCC (2006), IPCC guidelines for National GHG inventories 2006, chapter 3: Chemical Industry Emissions; http://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/3_Volume3/V3_3_Ch3_Chemical_Industry.pdf

OECD (2009), OECD integrated HPV database. Paris, Organisation for Economic Co-operation and Development; http://cs3-hq.oecd.org/scripts/hpv

PRODCOM (2009), http://www.eds-destatis.de/de/theme4/prodcom.php

REP (2009), Registre français des émissions polluantes (2009): http://www.pollutionsindustrielles.ecologie.gouv.fr/IREP/index.php

Roads2HyCom (2007), European Hydrogen Infrastructure Atlas *and* Industrial Excess Hydrogen Analysis, PART II: Industrial surplus hydrogen and markets and production; 2007

TUMünchen (2008), http://thor.tech.chemie.tu-muenchen.de/index.php?option=com_docman&task=doc_download&gid=340

UNFCCC (2009), http://unfccc.int/di/FlexibleQueries.do

Appendix A: Bulk organic chemicals

The term “bulk organic chemicals” is mentioned in the Annex I to the amended Directive and defines chemicals – as the name implies – by their production volume (bulk) and their origin (organic). APPE identified 25 petrochemicals belonging to this group. APPE defines petrochemicals (bulk organic chemicals) by the production of all products of steamcracker/PDH/Metathesis units and the associated chemicals as well as polymers which use a significant amount on a mole basis of one or more of the steamcracker/PHD/Metathesis products.

In chapter 2 we propose to use the 80/20 principle to determine which products are covered by product benchmarks and which by a fall back approach. Since the amended Directive says that benchmarking should be used to the “extent feasible” and the 80/20 principle is an attempt to limit the number of benchmarks, more products may be benchmarked (responsible for more than 80% of the total emissions of the chemical sector). The chemical industry, represented by Cefic, proposes further four (by-) products to be benchmarked:

- Ethylene dichloride / Vinyl chloride / PVC
- Ethylbenzene* / Styrene
- Ethylene oxide / Monoethylene glycol
- Cumene* / Phenol / Acetone

Since the developing of benchmarks for those products is linked with additional work and a proposal of the industry, the developing of benchmarks for those products is not in the scope of this report. Furthermore, two of the upper products are produced both in the refinery and the chemical sector. For such products we propose to use the CWT approach developed by CONCAWE, the representative of the refinery sector. Those corresponding products are marked with an asterisk.

The following approaches are exclusively quotes from the representatives of the corresponding chemical products and reflect exclusively their point of view. As explained above, we did not comment on those approaches. That is why there might be some parts which are not fully in line with our principles. The following text should show the advance of the sector work. The alternative approach for the upper products would be a fallback approach but the proposal to benchmark those products should be considered seriously. The following text should be regarded as a starting point for further discussion on whether and how to benchmark those products.

A.1 Ethylene dichloride / Vinyl chloride monomer

Background document on EDC/VCM manufacturing

Arguments for EDC/VCM benchmarking:

- 99.9% of VCM produced in the EU is manufactured by thermal cracking of EDC
- The manufacturing process of EDC and VCM is similar in all EU plants
- All VCM producers in the EU (except one) and the majority of EDC manufacturers are members of the European Council of Vinyl Manufacturers (ECVM), a sector group of PlasticsEurope
- ECVM members have a strong record of cooperation on issues pertaining to industrial hygiene, safety and the environment. The members of ECVM signed in 1995 the "ECVM industry Charter for the production of VCM and PVC" committing its members to reduce emissions and environmental impact of their manufacturing operations in general, with reference to BAT. In 2001, the members of ECVM further committed to continue improving resource consumption (material and energy use)
- ECVM members are used to participate to surveys in the framework of the eco-profile programme of PlasticsEurope.

EDC/VCM should be treated as a single entity in benchmarking, because:

- About 95% of EDC is used to manufacture VCM
- All VCM production in the EU takes place in combined EDC/VCM plants
- The processes are very much integrated in view of various recycling loops (especially hydrogen chloride produced by the cracking of EDC into VCM), and hence allocating energy consumption and CO_2 emissions specifically to EDC or to VCM would be very difficult and highly arbitrary
- Combined EDC/VCM plants are usually owned by the same companies and operated by a single crew

Table 19 EDC/VCM sites in EEA countries

Country	Company	Site	VCM capacity (kt/a)
Belgium	LVM	Tessenderlo	
	Solvin	Jemeppe s/ Sambre	
			970
Czech Republic	Spolana	Neratovice	
			135
France	Arkema	Lavera	
	Solvin	Tavaux	
	Vinylfos (Arkema)	Fos sur mer	
			1250
Germany	Solvin	Rheinberg	
	Ineos	Wilhelmshaven	
	Dow	Schkopau	
	Vestolit	Marl	
	Vinnolit	Gendorf	
	Vinnolit	Knapsack (Hurth)	
			2350
Hungary	Borsodchem	Kazincbarcika	
			400
Italy	Sartor	Porto Marghera	
	Sartor	Porto Torres	
			340
Netherlands	Shin-Etsu	Botlek	
			620
		Rafnes	
			500
Poland	Anwil	Wloclawek	
			300
Romania	Oltchim	Ramnicu Valcea	
			160
Slovakia	Novacke Chemicke Zavody	Novaky	
			95
Spain	Ercros	Vilaseca (Tarragona)	
	Vinilis and Hispavic (Solvin)	Martorell	
			500
Sweden	Ineos	Stenungsund	
			130
UK	Ineos	Runcorn	
			300
Total			**8050**

A.2 Styrene monomer

Introduction

The European Commission (EC) has issued a Directive in January 2008 initiating discussions on the allocation of CO_2 emission credits in support of the Emissions Trading System (ETS) after 2013. Industry groups such as the Association of the Petrochemical Producers in Europe (APPE) support a benchmarking approach for allocating CO_2 emission credits as being fair and an important tool in preserving the European competitive position. A mechanism to fairly allocate CO_2 emission credits is being sought. The EC has asked EU industries to provide robust, simple and verifiable CO_2 emission benchmarks for agreed petrochemicals.

The main objective of the APPE Energy Study Team (APPE EST) is to develop a benchmark for the ethylene plants (product High Value Chemicals) and to initiate the development of benchmarks for the other major petrochemicals. This paper describes the methodology which will be utilised to benchmark the highly important chemical intermediate Styrene Monomer.

Styrene Monomer

Styrene Monomer has been selected for benchmarking because it falls under NACE Code 2014 “Production of bulk organic chemicals by cracking, reforming, partial or full oxidation or by similar processes, with a production capacity exceeding 100 t per day”. Approximately 4.5 million metric t of Styrene Monomer are manufactured in EU27 annually.

Styrene Monomer is an aromatic hydrocarbon and the precursor to a vast number of polymer materials of major importance to the EU and global communities. The single largest outlet for Styrene Monomer is in the production of Polystyrene. Polystyrene is used in the manufacture of consumer articles such as packaging for food transportation and preservation, cups for hot beverage dispensing machines and items such as plastic cutlery and glasses. Polystyrene is also used in the manufacture of thermal insulation panels for buildings and construction. Polystyrene insulation foams are an essential technology which will help the EU Community to achieve its carbon and energy conservation targets.

Other important uses of Styrene Monomer include the production of housings for electrical goods such as computers and televisions, automotive parts and the turbine blades of wind powered generators, the latter being a major contributor to sustainable energy generation.

Styrene Monomer Production

There are 2 principal production processes for Styrene Monomer.

i) Dehydrogenation of Ethyl Benzene

Styrene Monomer can be produced by the catalytic dehydrogenation of Ethyl Benzene. Ethyl benzene is mixed in the gas phase with 10–15 times its volume in high-temperature steam, and passed over a solid catalyst bed. Steam serves several roles in this reaction. It is the source of heat for powering the endothermic reaction, and it removes coke that tends to form on the catalyst through the water gas shift reaction. The steam also dilutes the reactant and products, shifting the position of chemical equilibrium towards products.

A typical Styrene Monomer plant consists of two or three reactors in series, which operate under vacuum to enhance the conversion and selectivity. Selectivity to Styrene Monomer is 93-97%. The main byproducts are benzene and toluene. Because Styrene Monomer and Ethyl Benzene have similar boiling points (145° and 136 °C, respectively), their separation requires tall distillation towers and high return/reflux ratios.

ii) Via ethyl benzene hydroperoxide
Styrene Monomer is also co-produced with propylene oxide in a process known as Propylene Oxide – Styrene Monomer route. In this process ethyl benzene is treated with oxygen to form the ethyl benzene hydroperoxide. This hydroperoxide is then used to oxidize propylene to propylene oxide. The resulting phenylethanol is dehydrated to give styrene.

$$C_6H_5CH_2CH_3 + O_2 \rightarrow C_6H_5CH_2CH_2O_2H$$
$$C_6H_5CH_2CH_2O_2H + CH_3CH{=}CH_2 \rightarrow C_6H_5CH_2CH_2OH + CH_3CHCH_2O$$
$$C_6H_5CH_2CH_2OH \rightarrow C_6H_5CH{=}CH_2 + H_2O$$

Equation 27

Styrene monomer producers and EU regional capacities
The major European producers of Styrene Monomer are:

Company	Production Locations
BASF S.E.	Germany, the Netherlands
BAYER MATERIAL SCIENCE	the Netherlands
DOW EUROPE GmbH	the Netherlands
INEOS NOVA	Germany
LYONDELLBASELL	the Netherlands
POLIMERI EUROPA S.p.A.	Italy, U.K.
REPSOL QUIMICA S.A.	Spain
SHELL CHEMICALS EUROPE	the Netherlands
SYNTHOS DWORY	Czech Republic, Poland
TOTAL PETROCHEMICALS	Belgium, France

EU 27 styrene monomer production capacities (1000 t) for 2009 are estimated to be:

Belgium	500
Bulgaria	40
Czech Republic	170
France	600
Germany	640
Italy	625
Netherlands	1660
Poland	200
Romania	110
Spain	630
United Kingdom	60

The total estimated capacity is 5.235 million t.

Proposed Styrene Monomer production process CO_2 emission benchmarking study

The following data will be collected for a Styrene CO_2 Emission Benchmark study:

(a) CO_2 emission based on energy demand from process fuel, steam and electricity,

(b) Direct process emissions of CO_2 if any; all data per t of Styrene Monomer produced.

The APPE EST has engaged Philip Townsend Associates (PTAI), an expert consultant in this field, to support selected petrochemicals such as Styrene Monomer in developing the CO_2 emissions benchmark methodology, extracting historical data and in executing 2007/2008 European CO_2 benchmark studies as appropriate. The benchmarking study is being executed in 2 phases:

Phase 1 Methodology – Data Extraction from Existing Benchmarks

PTAI has compiled data taken from an existing database for an Ethyl Benzene/Styrene Monomer (EB/SM) benchmarking exercise conducted in 2005. The following table illustrates the t of CO_2 emissions per t of EB/SM production based on the available data.

Table 20 Specific CO_2 emissions emerging from the production of EB/SM

	EU average	Global average	Lowest 4 plant average
Fuel	0.362	0.465	-
Steam	0.398	0.358	-
Fuel + steam	0.760	0.823	0.611
Power	0.094	0.079	-
Total (Fuel+steam+power)	0.854	0.903	0.699

The units are in t CO_2/ t EB/SM and the conversions factors used were electricity 0.650 t CO_2/MWh; steam 0.062 t CO_2/GJ; fossil fuel 0.0568 t CO_2/GJ.

The simple average is being utilized as the industry average. The global simple average is also provided as a reference.

Where applicable, the simple average of the lowest 4 plants has also been provided.

Phase Two Methodology Overview - CO_2 Emissions Benchmarking

It is recognized that CO_2 emissions methodology must be adjusted to the characteristics of each individual product.

1. Agree with the SPA the list of styrene producers and plant sites to be benchmarked; the plant perimeters for both EB-SM producers and PO co-product styrene producers and the base years (2007 and 2008) of the comparison.
2. Agree on a mechanism for selecting a different base year or otherwise correcting for significant deviations from normal production at a particular plant during the base years. For instance, should catalyst cycle be considered rather than calendar years?
3. Agree exactly how to handle confidentiality issues, and gain legal advice for drafting any further confidentiality agreements which may be appropriate.

4. Based on work already executed on Phase One and in prior benchmark studies, develop input Data Documents to gather production, energy consumption, direct process emissions and any other relevant information. Separate Data Documents will be required for EB-SM and PO co-product styrene production.
5. Finalize the listing of all EU27 production plants for both processes. A responsible company contact individual is required for each production site. Determine how to handle participation, if any, from non-Cefic members.
6. Agree with the SPA exactly how the results from the two technologies will be combined in a meaningful way; to be used to develop confidential deliverables from the benchmark study.
7. Provide the appropriate confidentiality permission document to the companies managing all production plants, and gain agreement to participate in the benchmark program.
8. Estimate EU27 production during the base years for each product, using public data or market data from the Cefic product committee and cooperating European producers, as a consistency and completeness check.
9. Distribute the input Data Documents and provide support during the data collection production via email, telephone and teleconference as appropriate.
10. Collect and verify data required from individual producers for production, total energy demand and CO_2 emissions in EU27 during the base year. Keep the SPA informed on success of data recruitment efforts, so that a reasonable stopping point can be agreed upon. PTAI will strive to maximize participation.
11. Review results of combining technologies mentioned in Step 6 above, to ensure that a unique market, location, technology or other situation does not unfairly disadvantage other producers. Discuss and agree various such situations with the SPA.
12. Prepare industry curve(s) and draft report summarizing the study for review by the SPA.
13. Incorporate agreed revisions and publish final curve(s) and summary report according to the confidentiality guidelines.

Phase Two – Deliverables and Timing

For styrene produced by both processes, PTAI will provide curve(s) showing CO_2 emissions per t of product for the European industry on the agreed-upon basis, and a short summary report documenting calculations and related methodology issues which may have emerged.

Draft Phase Two results will be made available to the SPA by October 2009 and the finalized Phase Two results depending on when PTAI receives data and revisions from participants, are targeted for early December 2009 at latest

A.3 Ethylene Oxide / Mono Ethylene Glycol

Introduction

The European Commission (EC) issued a Directive in January 2008 initiating discussions on the allocation of CO_2 emission credits in support of the Emissions Trading System (ETS) after 2013. Industry groups such as the Association of the Petrochemical Producers in Europe (APPE) support a benchmarking approach for allocating CO_2 emission credits as being fair and an important tool in preserving the European competitive position. A mechanism to fairly allocate CO_2 emission credits is being sought. The EC has asked EU industries to provide robust, simple and verifiable CO_2 emission benchmarks for agreed petrochemicals.

The main objective of the APPE Energy Study Team (APPE EST) is to develop a benchmark for the ethylene plants (product High Value Chemicals) and to initiate the development of benchmarks for the other major petrochemicals such as Ethylene Oxide and Ethylene Glycol (EO-EG).

Ethylene Oxide Production

Ethylene Oxide is a basic petrochemical and precursor to a large number of solvents, amines, surfactants and related materials, as well as its largest outlet worldwide, mono-ethylene glycol. There is about 2.7 million t of ethylene oxide capacity in Europe, produced by the oxidation of ethylene over a silver catalyst typically with pure oxygen. An important consideration in EO manufacture is the extreme reactivity of the EO molecule, which has resulted in a number of severe industrial accidents historically.

The largest single use for ethylene oxide is to produce ethylene glycol. Other important uses are ethanol amines, ethylene amines, oxygenated solvents such as glycol ethers, other specialty solvents and surfactants, as well as minor medical and food industry applications.

Ethylene Glycol Production

The largest volume product based on ethylene oxide is mono-ethylene glycol, which is mainly used to produce automotive anti-freeze and polyester. Polyester is typically produced from terephthalic acid and mono-ethylene glycol. There is about 1.5 million t of ethylene glycol capacity in Europe, produced by the hydrolysis of ethylene oxide. Large capacity increases in the Middle East in recently years have disadvantaged European producers.

Polyester provides an important fiber for clothing and a wide variety of other textile applications. Polyester resin or more properly poly-(ethylene terephthalate) (PET) is an important packaging material widely used for water and soda bottles, as well as juice drinks and a variety of related packaging applications.

EO & Derivatives Producers and EU Regional Capacities

European producers of ethylene oxide and ethylene glycol are:

AKZO NOBEL
ARPECHIM
BASF S.E.
CLARIANT
DOW EUROPE GmbH
INDUSTRIAS QUIMICAS
INEOS
LUKOIL
POLISH KONCERN NAFTOWY ORLEN
SASOL
SHELL CHEMICALS EUROPE
SLOVNAFT

Estimated EU 27 Ethylene Oxide 2009 production capacities (1000 metric t):

Belgium	660
Bulgaria	90
France	200
Germany	920
Netherlands	550
Poland	90
Romania	40
Slovakia	40
Spain	100

The total European estimated capacity of ethylene oxide is about 2.7 million t.

Estimated EU 27 Ethylene Glycol 2009 production capacities (1000 metric t):

Belgium	370
Bulgaria	100
France	90
Germany	410
Netherlands	330
Poland	100
Romania	30
Slovakia	40
Spain	90

The total European estimated capacity of ethylene glycol is about 1.5 million t.

Proposed Ethylene Oxide-Ethylene Glycol CO_2 emission benchmark study

The following data will be collected for the Ethylene Oxide-Ethylene Glycol CO_2 Emission Benchmark study based on the last complete catalyst cycle:

(a) CO_2 emissions based on energy demand from process, fuel, steam and electricity, calculated using agreed factors for conversion to CO_2-equivalents. A thorough and complete energy balance is required to adequately and fully benchmark the ethylene oxide and ethylene glycol processes, both of which are exothermic. Particular emphasis will be placed on properly collecting the energy demand associated with steam usage, specifically temperatures, pressures and quantities for each level of steam utilized in the process and/or exported from the process. The energy demand from steam usage will also be calculated from the inputs and compared against the reported values as a cross check in data validation.

(b) Direct process emissions of CO_2 as generated from the oxidation of ethylene ("burn") as related to catalyst selectivity varying through the catalyst cycle, and corrected for CO_2 recovery into approved uses;

(c) Raw materials including ethylene and oxygen

(d) Ethylene oxide produced and;

(e) Ethylene glycol produced including all products manufactured in the process: Mono-ethylene Glycol (MEG), Di-ethylene Glycol (DEG), Tri-ethylene Glycol (TEG) and other heavier glycols.

All CO_2 emissions data will be presented per t of ethylene oxide equivalent (EOE) produced.

Methodology Overview - CO_2 Emissions Benchmark

Calculation of CO_2 emissions for EO-EG will be adapted for the following special factors, which must be reviewed and accepted by the producers' Technical Team and are incorporated into the benchmark project execution steps numbered below:

- Differences in catalyst selectivity and catalyst life cycle – During plant design, producers choose their optimum catalyst selectivity based on desired length of production run and relative costs of ethylene and energy. CO_2 emissions calculation on a catalyst cycle rather than a calendar year basis is more meaningful since catalyst selectivity varies throughout the cycle, which can extend to two years or more. The base period for the benchmark for each producer will be their most recently completed catalyst life cycle that ended during 2007 and 2008. A further mechanism may be required to adjust if a producer has not completed a catalyst life cycle in the period January 2007 to December 2008. Catalyst selectivity must be reported for various points in the catalyst life cycle.
- Process CO_2 emissions vary throughout the catalyst life cycle. The ethylene "burn" energy which leads to the process CO_2 emissions, substitutes for external energy inputs (typically steam). Ethylene "burn" energy is typically recovered as internally generated steam that is utilized within the EO-EG process boundaries. In effect;

increasing process CO_2 emissions during the catalyst cycle are offset by reducing CO_2 emissions for direct energy inputs. These balancing effects must be captured throughout the catalyst life cycle.

- CO_2 quantities generated by the EO-EG manufacturing process will also be calculated and compared against the reported values as a cross check during data validation. Process CO_2 emissions are recaptured into approved uses by some producers.
- EO-EG Product Mix – Some units produce pure EO to supply downstream units making a full range of other derivatives but only minimal amounts of by-product ethylene glycol. Other units produce varying amounts of EG up to the full EO capacity with no other derivatives made. An approach to put all saleable products on an equivalent basis is needed (ethylene oxide equivalents or EOE). If pure EO is to be used to produce other derivatives or for direct sales, an additional EO purification step is needed, which can be minimized if only EG is produced. Adjustments will be made as necessary for EO-Only and EG-Only producer sites. The CO_2 calculation will be based on actual product mix sold, on an EOE basis with actual (direct energy + indirect energy + process CO_2 emissions) reported, as t CO_2/t EOE.
- Accounting for effect of different and partially interchangeable energy carriers on the specific CO_2 emissions – Agreed CO_2 emission factors for the various energy carriers will be used to convert all energy and CO_2 process emission flows into equivalent CO_2 t/t product EOE for each production unit. The industry supply curve(s) developed as described under the Deliverables section will be then used to rank order the production units on that basis.
- Plant perimeter and related facilities – Ensure that flares and storage facilities are treated in the same way by all producers. Each major process stream and utility flow will be collected and validated for CO_2 emissions calculation. See the attached flow diagram. Catalyst reprocessing and oxygen supply are energy intensive but considered outside the plant perimeter and off-site for this study.

A.4 Cumene / Phenol / Acetone

Phenol Information from the European Phenol Sector Group to the Ecofys/Fraunhofer Institute concerning the ETS post 2012 Sector Report for the Chemical Sector.

Background

The following table lists all phenol, acetone and cumene production sites in the EU as well as their location, company, capacity and number of production lines.

Table 21 EDC/VCM sites in EEA countries

Country	Company	Capacity (kt/yr)	Number of production lines	Location	Products[1]
Belgium	Ineos Phenol	680 / 420	2	Antwerpen	P / A
Germany	Ineos Phenol	660 / 410	1	Gladbeck	P / A
	Domo	150 / 95 / 200		Leuna	P / A / C
	Ineos	275		Marl	C
	BP	500		Gelsenkirchen	C
Spain	Ertisa	570 / 350 / 470		Huelva	P / A / C
Italy	Polimeri	480 / 300 / 640		Montova, Porto Torres	P / A / C
Netherlands	Dow	700		Terneuzen	C
Finland	Borealis	190 / 120 / 230		Porvoo	P / A / C
France	Novapex	155 / 95 / 230			P / A / C
Romania	Petrobrazi	75 / 45		Brazi	P / A
	Carom	25 / 15		Borzesti	P / A
Poland	Orlen	60 / 35 / 55		Plock	P / A / C
Slovakia	Slovnaft	50 / 30 / 112		Bratislava	P / A / C
Czech Republic	Deza	12 / 7		Vallaske-Mezir	P / A
Total EU 27		**3095 / 1922 / 3412**			**P / A / C**

[1] P = Phenol, A = Acetone, C = Cumene

The table is only indicative and without prejudice. It possibly contains units, which are part of refineries. For this survey we should only look at these units, which are in the chemicals sector. Those who are part of the refineries may be dealt within the refinery benchmark. Further investigation is being done by July 24th 2009.

Production Processes

General overview

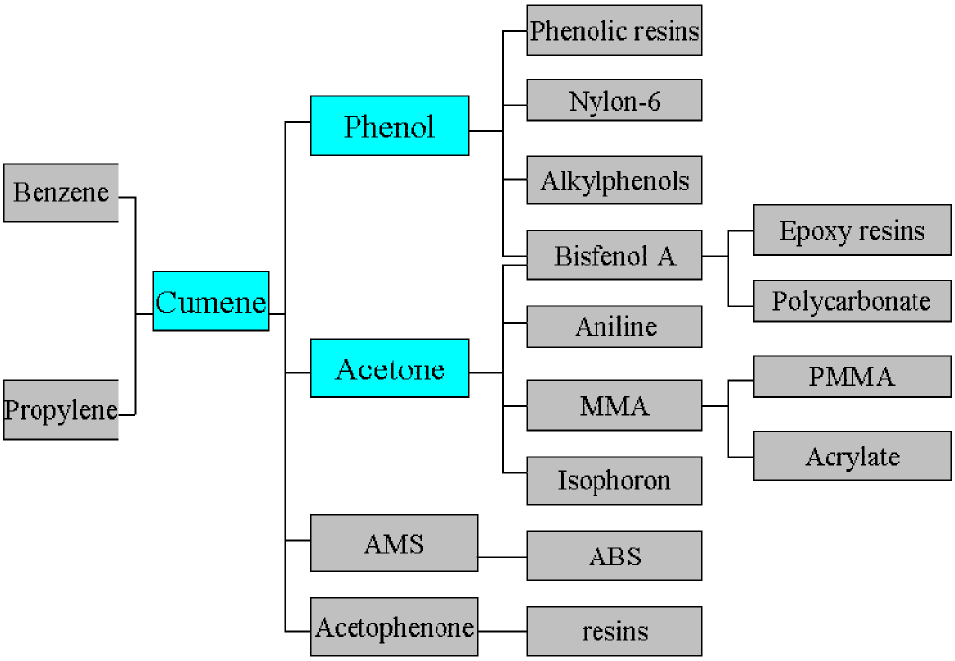


Figure 18 Derivatives from the production of Cumene, Phenol and Acetone

Most of the phenol production is used for the production of bisphenol-A, which is especially used for the production of high-grade polycarbonates for compact discs, for glazing, and for the automotive industry. Bisphenol-A is also used for the production of epoxy resins.

The second largest consumption of phenol is for the production of phenolic resins with formaldehyde. They are mainly used for underseal applications in the automotive industry. Phenol is also used for the production of caprolactam via cyclohexanol-cyclohexanone.

Many other derivatives from phenol are produced, such as aniline, alkylphenols, diphenols, and salicylic acid.

Cumene production process

Cumene is produced by acid catalysed alkylation of benzene with propylene. Earlier processes are based on heterogeneous solid Phosphoric Acid (H_3PO_4) catalyst or homogeneous aluminium chloride ($AlCl_{3)}$ catalyst. The new processes are based on fixed bed zeolite catalysts, causing less corrosion and by-products enabling better yields compared to the old types. The alkylation is an exothermic process. In addition to the alkylation a couple of distillation steps and in the zeolite process a trans-alkylations step are included in the process scheme.

Cumene is produced almost exclusively (98%) for the production of phenol and acetone.

Today, among others Badger Licensing, UOP, ABB/Lummus, Polimeri Europe, are licensing cumene technology.

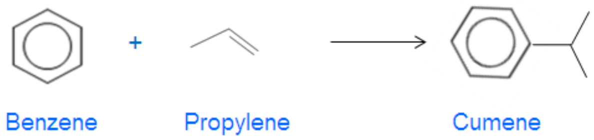


Figure 19 Structural formula of the cumene production

Phenol production process

Phenol and co-product acetone is produced via a two-step process starting with cumene (*Hock process*). In the first step, cumene is oxidised with normal or enriched air to form cumene hydroperoxide. This is an auto-catalytic oxidation. The hydroperoxide is then concentrated and subsequently decomposed (cleaved) by acid-catalysed rearrangement into acetone and phenol. The catalyst is subsequently removed and the reactor effluent neutralised before being sent to the distillation unit. High purity phenol and acetone is obtained in a series of purification steps, which may include hydro-extractive distillation, catalytic treatment, and extraction with caustics. By-products alpha-methyl-styrene and acetophenone are sometimes recovered as useful products, but alpha-methyl-styrene can also be hydrogenated to cumene.

There are two alternative commercial technologies for acid-catalytic cleavage of cumene hydroperoxide into phenol and acetone.

- cleavage in phenol/acetone medium, where the heat of reaction is removed by evaporation of acetone, i.e., the 'boiling process' (isothermal process)
- cleavage in phenol/acetone medium, where the heat of reaction is removed by cooling water, typically supplied to the tube-side of a heat-exchanger reactor (non-isothermal process)

The first process is essentially a heterophase process that occurs in a liquid/vapour system, while the second process is a single-phase homogeneous process.

Although the chemical reactions taking place in these two processes seem to be similar, the processes are in fact fundamentally different. The differences are not only the heat removal methods, but also equipment, level of process-integration, and control methods differ.

Today, among others ABB/Lummus (USA), Illa (Russia/USA), Mitsui (Japan), UOP (USA), and Kellogg (KBR, USA) license phenol/acetone production technology based on cumene oxidation. Some companies apply their own technology.

Simplified chemical reactions in phenol and acetone production:

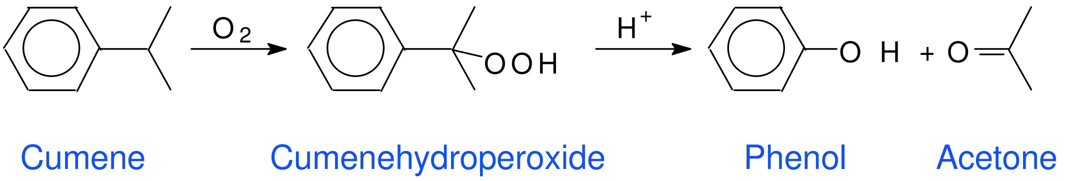


Figure 20 Structural formula of the phenol and acetone production

Final Proposal for products to be distinguished

- Phenol / Acetone / Cumene production is connected to NACE code 20.14 (Manufacture of other organic basic chemicals, with a production capacity of more than 100 t per day), as mentioned in Annex 1 to the amended Directive.
- As acetone is a co-product from phenol, both products should be considered together. Cumene on the other hand should be taken apart from phenol/acetone. Not all phenol/acetone producers have a cumene production plant integrated in their overall process chain.

Activities undertaken by the Phenol Sector

A work group within the Phenol Sector is being established with technology and energy/CO_2 specialists from each company, to come up with a benchmark value for both the phenol/acetone and cumene process.