Background document prepared by the Lower Olefins Sector Group of CEFIC on the BAT conclusions for lower olefins in the LVOC BREF

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Revision number 1

1. Introduction

In the summer of 2013, the EIPPCB submitted a questionnaire to all European cracker operators to collect data on emissions and on techniques used to abate emissions. The basis for this questionnaire was the BDQ document, prepared by I. Clenahan (Base Document for Questionnaire Latest revision: 18.01.2013, no final version issued).
The questionnaire included the request for data on the following topics:

- Emissions to Air
- Furnaces
- Acid gas removal
- Fugitives
- Catalyst regeneration
- Emissions to Water (De-coking, Dilution steam, Acid gas removal)
- Raw material consumption
- Energy consumption
- Water consumption
- Byproducts and waste
- Noise and vibration

The members of Lower Olefins Sector Group (LOSG) sent the completed questionnaires to EIPPCB and in parallel to CEFIC. CEFIC then asked an independent consultant (Prof. Dr.-Ing. W. Kaiser at the Hochschule Kaiserslautern, Germany) to analyze the questionnaires data .The objective of this data analysis was the deduction of Best Available Techniques Associated Emission Limits (BAT-AEL), in particular on the NOx and CO emissions of the cracker furnaces and on dust emissions during decoking.

This document summarizes the industry conclusions from this analysis.

2. Data collected via the questionnaire

In total, 42 steam cracker plants responded to the questionnaire. These plants submitted data for 489 individual furnaces. The average fired duty of these furnaces was about 50 MW.
For some furnaces, more than one emission data set was supplied, corresponding to different operation modes, (e.g. different feedstock, different cracking severity,…) so that in total 701 data sets were received for normal operating conditions. For the analysis of NOx and CO emission data, only the highest data point per furnace was retained.
Not all crackers filled in all data in the questionnaire. For instance, NOx data were provided for only 412 furnaces.
A cracker typically contains several furnaces of the same type (size and design). These furnaces are identical and therefore emissions are the same. In addition, furnaces often have a common stack. Figure 1 gives a breakdown of the set of data points for NOx emissions. The top graph shows how many furnaces have a dedicated emission measurement and whether measurement is continuous or spot. The bottom graph shows same information but per furnace type rather than per individual furnace.

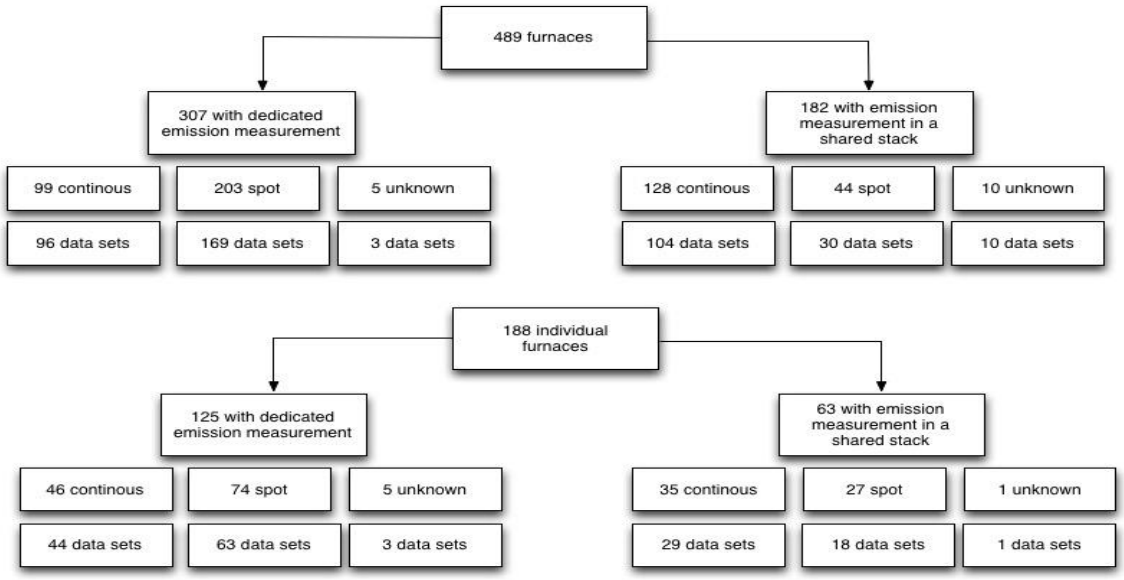

Figure 1: breakdown of data set for NOx emissions.

3. Contribution of NOx emissions of crackers to EU NOx emissions

Based on questionnaires, the average NOx emission per furnace is 3.8 kg/h. Multiplying by the total number of furnaces, this gives yearly emissions in the order of 16 kton/year. This should be compared to total NOx emissions in EU-28 of about 9.2 Million ton per year in 2010 (source: website of European Environmental Agency). The total contribution of EU ethylene crackers represents therefore less than 0.2 % of the EU NOx emissions. This is shown in more detail in Figure 2.

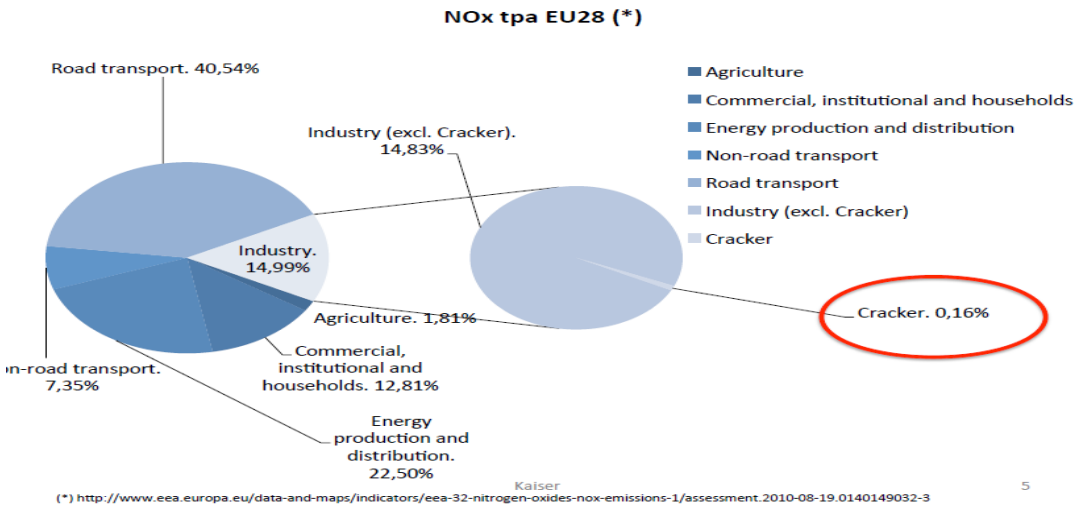

Figure 2: contribution of NOx emissions from crackers to overall EU NOx emissions.

4. Continuous emission monitoring.

Emissions monitoring by itself is not a technique that reduces emissions. Moreover, for maximum energy efficiency, furnaces are controlled on O2-excess, not on NOx emissions. NOx emissions will be the result of the O2 excess control point as is illustrated in Figure 9.

Local permitting authorities currently accept predictive emissions models and/or periodic or spot emissions measurements as reliable alternatives for reporting steam cracker furnace emissions data.

The LVOC BREF D1, section 4.4.1.1.2 claims that continuous measurement results in lower emissions than periodic or spot measurement. The conclusion is based on a selective set of furnaces and is misleading. The difference in lower emission values for continuous measurement as claimed in LVOC BREF D1 is actually due to other factors such as age, type of furnace, firing density. (The majority of furnaces equipped with a dedicated continuous measurement are new, hence equipped with state of the art burners, giving lower emissions).

To illustrate this, Figures 3a-b compare emissions from furnaces with standard burners, respectively staged air or fuel burners. In contrast to the data reported in the LVOC BREF D1, these data sets contain also emission data of furnaces connected to a common stack.

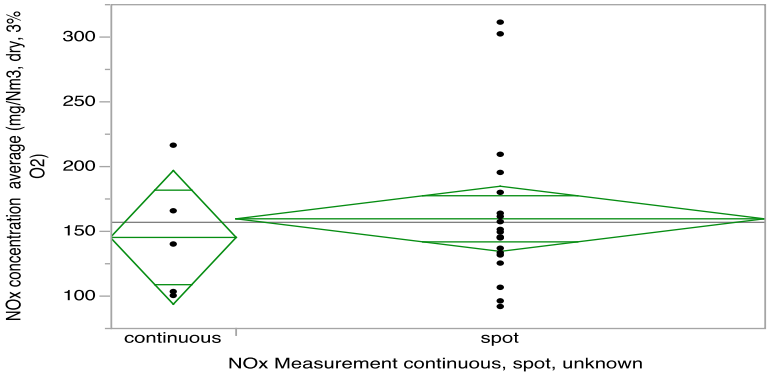

Figure 3a: comparison continuous versus spot measurements for standard burners

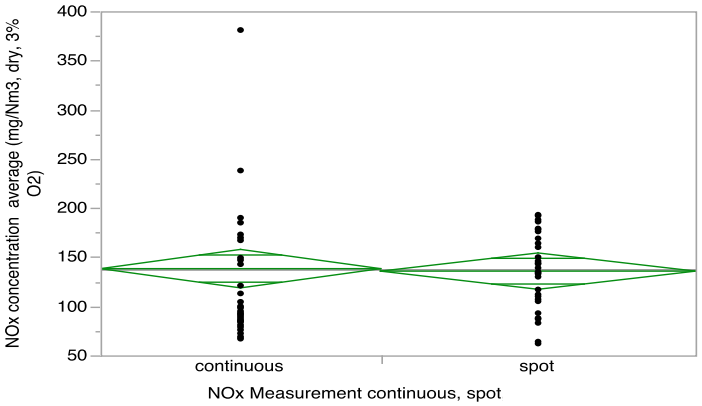

Figure 3b: comparison continuous versus spot measurement for staged air or staged fuel burners.

The vertical span of the diamonds in these graphs shows the 95 % data confidence interval. The diamond width represents the data sample size. The middle horizontal line across each diamond represents the group average. Overlapping diamonds indicate that the two group means are not significantly different.

If the statement that continuous monitoring should lead to lower emissions would be correct, this should result in non-overlapping diamonds in figure 3a-b which is not the case.

Moreover, for furnaces having small variations in NOx emissions, little benefit is expected from continuous emission monitoring.

Finally yet importantly, the LCP BREF and REF BREF do not call for continuous measurement for combustion units < 50 MW and the REF BREF, allows for indirect measurements of NOx (eg PEMS) as an applicable BAT for furnaces with duty between 50 MW and 100 MW.

Industry position 1: Continuous emissions monitoring is not the only possible BAT for emissions monitoring. Predictive emission models or periodic spot measurements with a frequency to demonstrate that BAT-AEL limits are respected are valid alternative BAT technologies.

5. BAT-AEL Averaging period.

Figure 4 and 5 respectively show the average, maximum and minimum NOx and CO emissions of the whole furnace population per furnace. These figures give an impression of the variability of the emissions of individual furnaces.

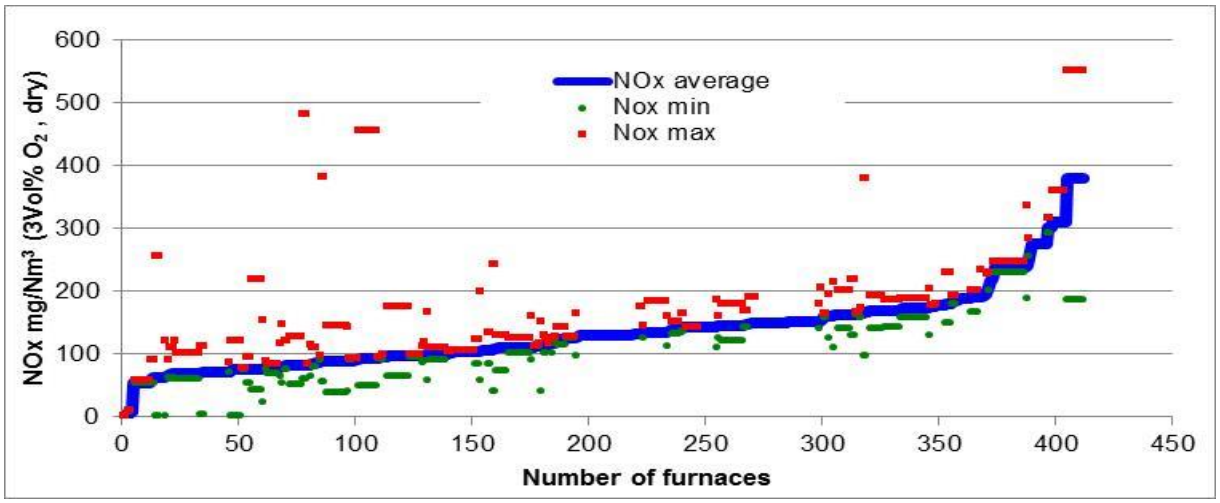

Figure 4: Variability of NOx emissions of all furnaces

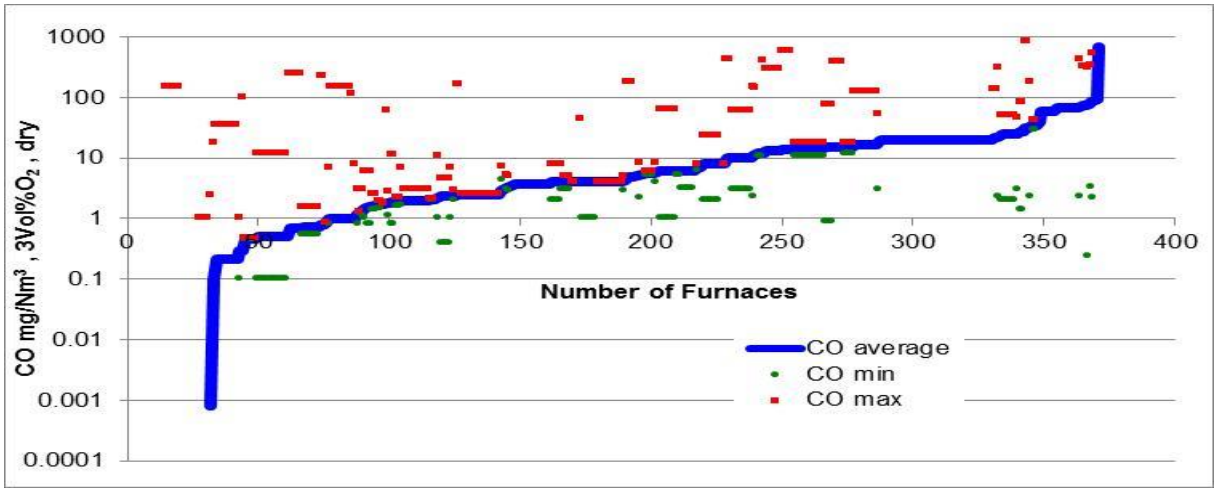

Figure 5: Variability of CO emissions of all furnaces

The industry sector judges that a yearly averaging period is appropriate to cover for this variability and avoids establishing significantly extended ranges for BAT-AEL daily averages.
In this yearly average, periods of other than normal conditions (eg. decoking operations) should be excluded. Monitoring should consist of regular spot measurements, the frequency of which will be sufficient to demonstrate that emissions are below the upper BAT-AEL (monthly, quarterly, every 6 months, yearly...).
Increased monitoring may be organized when (NOx) emissions vary in a wide range and when emissions will go beyond the upper BAT-AEL yearly average to identify mitigation steps.

Industry position 2: BAT-AEL emission levels should be on a yearly average basis

6. SCR

Installation of SCR on steam cracker furnaces has a high cost. On existing furnaces, the applicability of SCR may be limited due to the requirements for significant space and optimal reactant injection.
SCR installation also results in additional NH3 emissions, in additional operating costs (chemicals and catalyst) while alternative techniques (burner modifications) may achieve comparable emissions performance (see Figure 6).

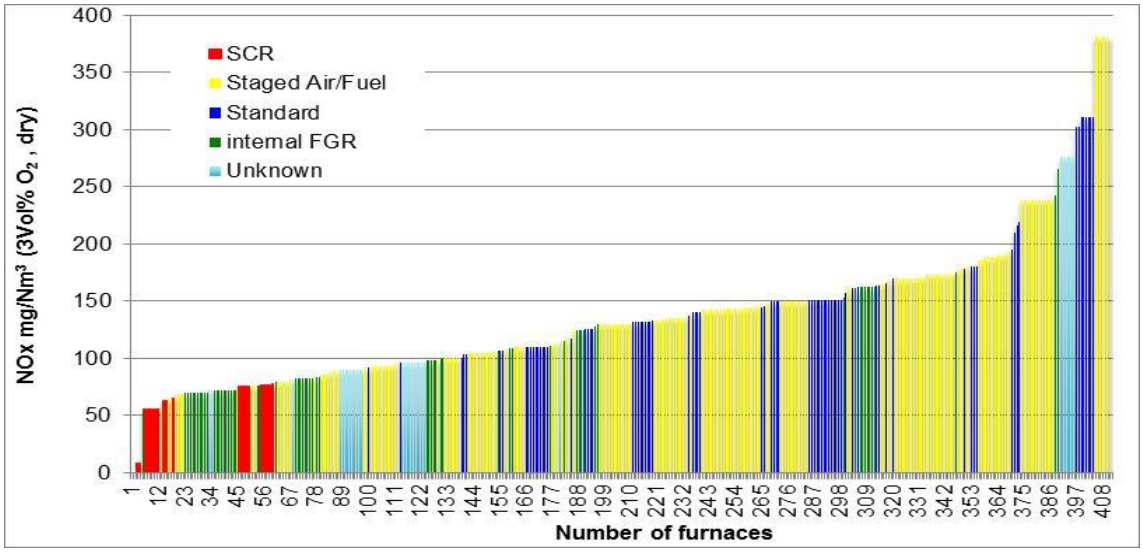

Figure 6: **Steam cracker furnace NOx emissions categorized per NOx abatement**

It is also interesting to note that the last SCR on a new furnace was built in 2001 (the last SCR on a revamped furnace was installed in 2012).

Industry position 3: SCR is BAT generally applicable to new ethylene cracking furnaces if cost effectiveness criteria are met. It needs to be assessed if the additional reduction of NOx emission by SCR as compared to for example low NOx burners justifies the incremental investment and operational cost. SCR is generally not applicable to existing ethylene cracking furnaces due to ducting configuration, space availability, chemicals installation safety and very high cost to environmental benefit compared to low NOx burner technology

7. BAT-AEL for NOx emissions during normal operations.

The BAT-AEL should reflect a realistic emissions target considering what abatement improvement could (still) be made while avoiding an excessive cost impact.

The industry sector judges that application of low NOx burner technology (either staged air or staged fuel or with internal flue gas circulation) is best available technology to reduce NOx emissions. Low NOx burner technology here is used as a generic term covering also ultralow NOx burners.

Figure 7 shows NOx emissions of existing furnaces equipped with low NOx burner technology. Data for SCR are also included. However, as explained in paragraph 6, SCR is not generally applicable to existing furnaces. The industry sector therefore judges that these values should not be taken into account in determining the normal range of BAT-AEL values for NOx, but be treated via a footnote in the BAT-AEL table.

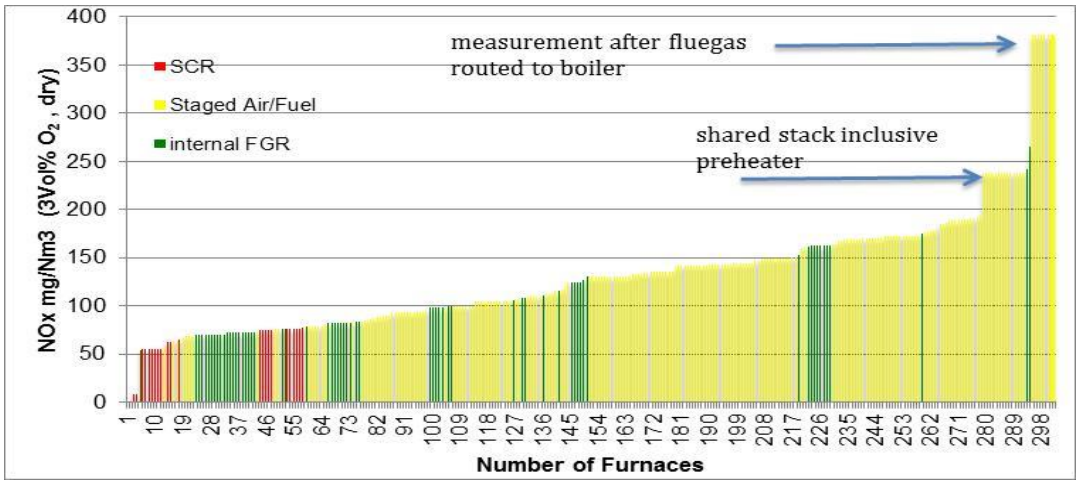

Figure 7: average NOx values for furnaces equipped with BAT technology for NOx emissions reduction.

Figure 7 shows that NOx emissions span a range of about 50 to about 190 mg NOx/Nm3, excluding the two higher plateau values at 240 mg/Nm3 and 350 mg/Nm3. These latter values correspond to specific cases not representative for the broader furnace population (the value of 240 mg/Nm3 concerns furnaces with a shared stack to which a superheater is connected. The value of 350 mg/Nm3 concerns furnaces whose flue gases are routed to a boiler).

On the lower end of the range, only the SCR technology is able to guarantee values consistently below 80 mg/Nm3, but as explained in paragraph 6, SCR is not a generally applicable BAT. The other low NOx technologies are not able to consistently guarantee values below 100 mg/Nm3. This is because several parameters such as furnace layout, firing density, fuel gas composition, cracking severity, arch temperature affect NOx emissions.

Based on the analysis of the NOx emissions data in Figure 7, the industry sector proposes to set the lower end of the BAT-AEL range at 100 mg/Nm3 and the higher end of the BAT-AEL range at 200 mg/Nm3 and to add footnotes that higher values and lower values are possible in specific cases.

For new furnaces, Figure 8 shows the NOx emissions data of 11 furnaces constructed after 2007. This figure shows an emissions range between 80 and 100 mg NOx/Nm3, except for one furnace with NOx emissions at 130 mg/Nm3. This furnace was constructed in 2007 and the NOx burner vendor guaranteed an emission of 100 mg NOx /Nm3. The industry sector considers that, since 2007, knowhow of burner vendors has increased such that an emissions range of 80-100 mg NOx/Nm3 for new furnaces is a realistic expectation. No furnaces with SCR are included: as stated in paragraph 6, there are no new furnaces with SCR constructed since 2001.

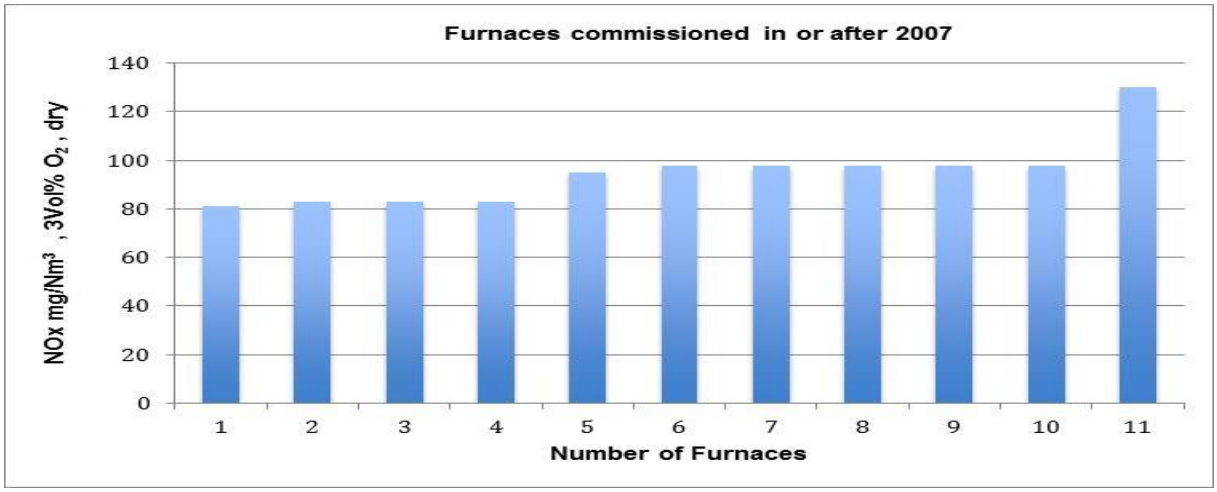

Figure 8 : NOx emissions for new furnaces (built after 2007) equipped with low NOx burner technology.

Finally, BAT-AEL values for NOx should relate only to normal operation conditions. Values during decoking may be higher, as the furnace is operated at very low loads during this phase (as low as 15 % of normal operating firing duty). Due to the limited period of decoking during the year (see paragraph 11) as well as low firing duties, the total yearly NOx emissions during decoking operations compared to the total yearly NOx emissions of normal operations are negligible.

Industry position 4: BAT-AEL for NOx during normal operations should be based on application of low NOx burner technology (either staged air or staged fuel and/or with internal flue gas circulation).
The following yearly average NOx BAT-AELs during normal operation are proposed:

	Min NOx (mg/Nm3, 3 Vol% O_2, dry)	**Max NOx (mg/Nm3, 3 Vol% O_2, dry)**
Existing furnaces	100(*1)(*2)	200(*3)
New furnaces	80 (*4)	100 (*3)

(*1) Lower values are achievable under specific conditions (firing density, fuel gas composition, low furnace load) and with low NOx burners, but are not always guaranteed

(*2) Values in the range 60-80 mg/Nm3 are achievable with SCR. However, this technique may not be applicable (industry position 3). Moreover, for revamps, cost effectiveness of SCR versus Low NOx burners should be considered for determination of BAT.

(*3) Integrated furnace configurations with improved overall energy efficiency (use of air preheat, use of turbine exhaust gas, furnace from which flue gasses are routed to a boiler etc.) may have NOx emissions that fall outside this BAT-AEL range (re BDQ section 2.1.3.4). The NOx emission of such configurations shall be limited to the calculated BAT-AEL emission based on the total fire duty of the corresponding individual sources in a non-integrated configuration.

(*4) For new furnaces values around 60 mg/Nm3 can be attained via SCR, but this technology may not be cost effective with respect to other BAT technologies. It needs to be assessed if the additional reduction of NOx emission by SCR as compared to for example LNB justifies the incremental investment and operational cost.

8. BAT-AEL for CO during normal operations.

CO, NOx and O2 excess levels are intimately linked as shown in Figure 9. Reducing excess air below 10% to minimize NOx emissions and energy consumption will drastically increase CO emissions.

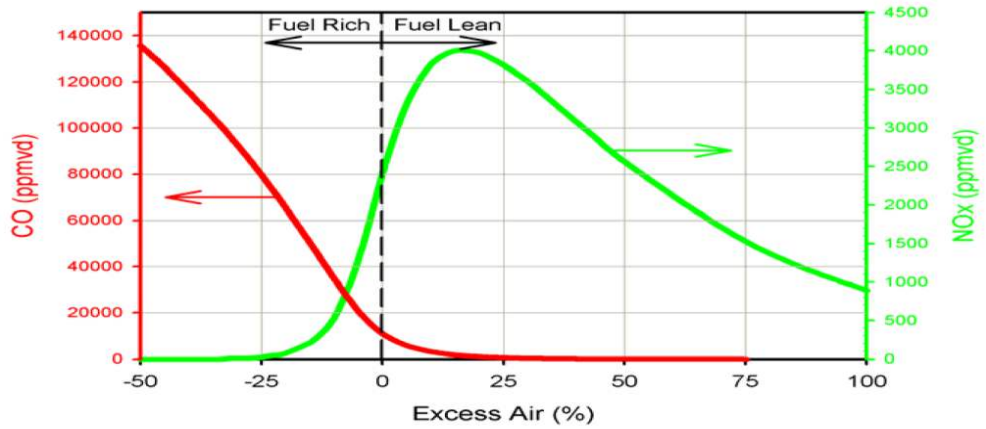

Figure 9: Adiabatic equilibrium NO and CO as a function of the Excess Air
(Simulator for Teaching Process Heater Operating Principles : C. Baukal, Ph.D., P.E. and W. Bussman, Ph.D. John Zink Company, LLC)

Given the impact on NOx emissions and energy consumption determining a realistic BAT-AEL for CO is not obvious.
Figure 10 shows the reported average CO concentrations for furnaces having installed BAT technology for NOx reduction, being able to achieve low CO emissions.

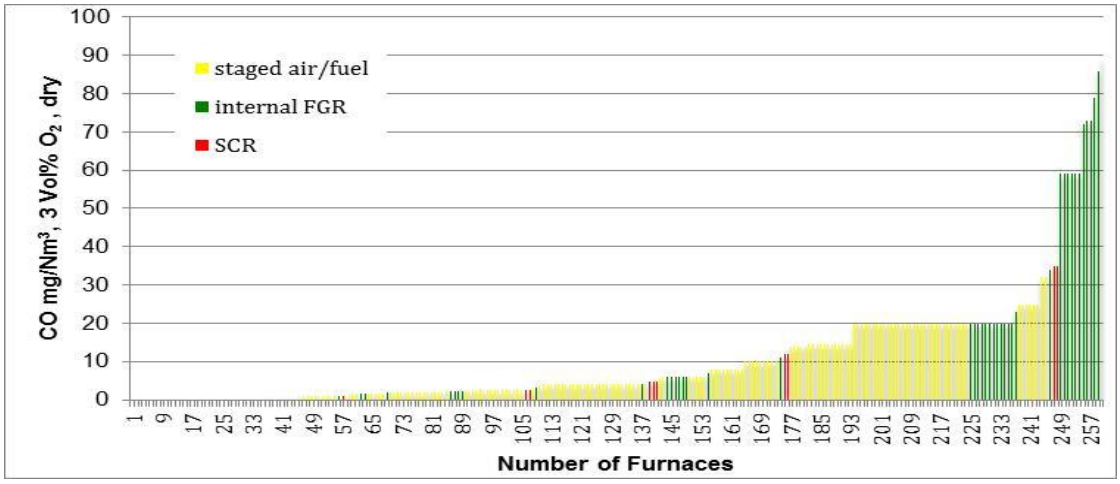

Figure 10: Steam cracker furnace average CO emissions for furnaces equipped with low NOx burner technology.

Based on these considerations and consistent with the logic of the LCP BREF, the industry sector proposes that no BAT-AEL values for CO are imposed and that values listed in the BAT conclusions would be indicative only.

Industry position 5: There should be no BAT-AEL for CO during normal operation. The following yearly average indicative values for maximum CO emissions are proposed:

	Indicative value for average CO emissions (mg/Nm3, 3Vol% O_2, dry)
New and existing furnaces	< 90

9. BAT-AEL for particulate matter (PM) during normal operations.

More than 95 % of the steam cracker furnaces burn only gaseous fuels with inherent minimal dust emissions. These low dust emissions do not justify the installation of any abatement technology.

Although 47 operators indicated in the questionnaire to have done some flue gas PM measurement only one operator provided data for normal operations representing 7 identical furnaces burning a mixture of liquid and gas, reporting as low as 2.7 mg PM /Nm3.

Industry position 6: No BAT-AEL for PM in flue gas for normal operations for gas fired furnaces.

10. BAT-AEL for SOx

Typically the fuel gas burned in steam cracker furnaces is produced by the cracker itself (sometimes supplemented with Natural Gas or LPG), containing very low quantities of sulfur.

Even the furnaces, which also burn liquid fuel, typically only use the pyrolysis fuel oil that is low in Sulfur (typically less than 0.3 %wt S) compared to typical refinery streams. Yearly reported emissions can therefore be based on evaluation of sulfur in the liquids being used (re LVOC BREF D1 BAT 2).

The questionnaire data on sulfur emissions confirm low emissions (Figure 11).

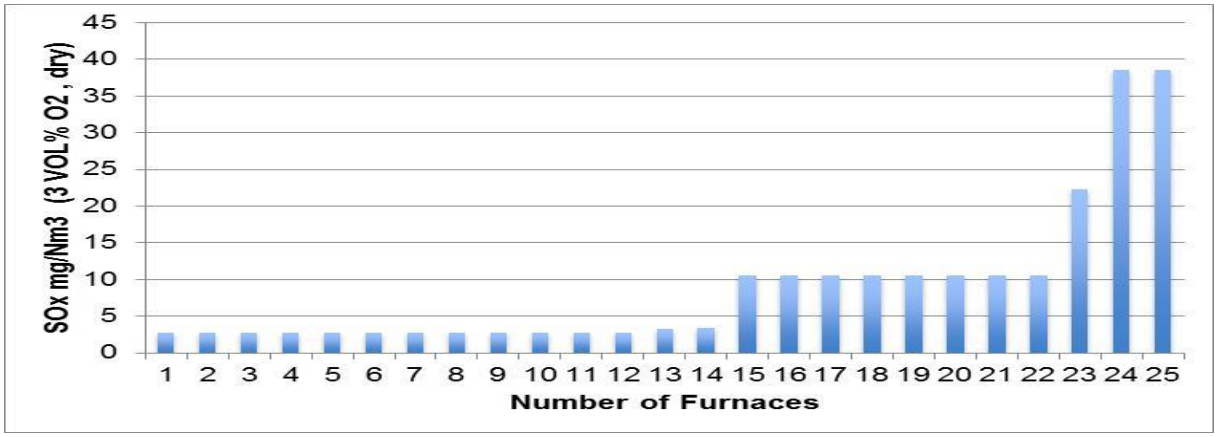

Figure 11: furnace sulfur emissions during normal operation.

Industry position 7: No BAT-AEL for SOx emissions during normal operations

11. BAT-AEPL for dust emissions during decoking

Decoking should be regarded as other than normal operations. It is only done during a limited amount of time and with a frequency that are both already minimized to maximize the furnace availability for ethylene production.

Figure 12 shows that decoking is done only an average of 3% of the total runtime of a furnace per year.

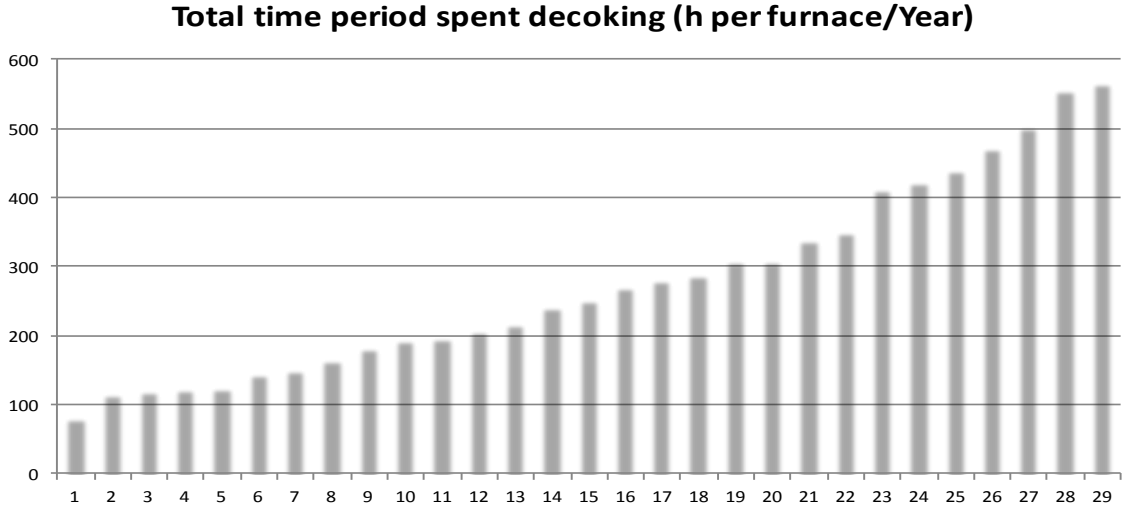

Figure 12: Typical decoking time per furnace and year (given is the time for one typical furnace per cracker).

The decoking operation also typically only lasts between 12 and 48 hours during which the dust concentration has a relatively short and limited peak value. See Figure 13.

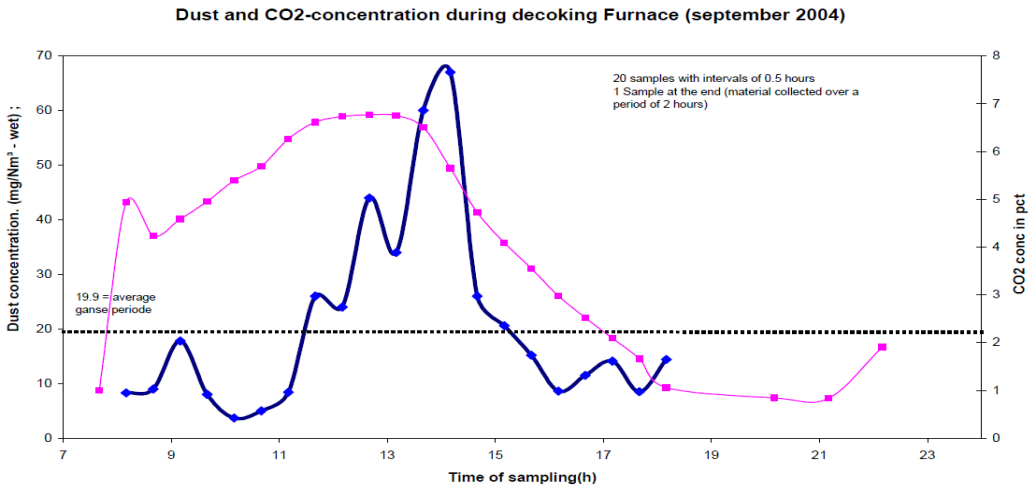

Figure 13: Example of dust concentration trend during furnace decoking.
The blue curve is the dust concentration measured during the cycle (measured on left), the purple curve the CO2 (axis on right)

Combining figures 12 and 13, it can be concluded that decoking results in limited dust emissions less than 50 hours per year per furnace.

The measurement of dust emissions during decoking is complicated and requires a standard. Such a standard would have to consider the presence of solid particles and large amounts of steam, the timing of the sampling and the specification of an isokinetic sampling system for measuring dust emissions during highly fluctuating decoking conditions. So far, such a standard is lacking and hence it is not surprising that only a limited number of cracker operators provided feedback on their dust emissions during decoking and the dust emission data points show a huge variation. On a wet basis the following data were submitted in the questionnaire are as shown in Figure 14.

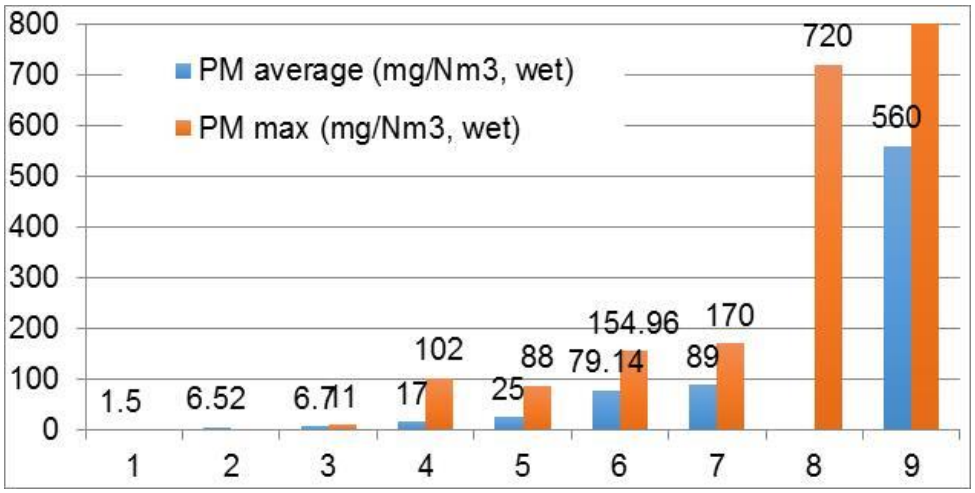

Figure 14 : Feedback from questionnaire concerning dust emissions.

Given all these considerations the industry sector feels that the BAT-AEPL as included in the LVOC BREF D1 (BAT 35) is not appropriate and should be removed. In any case, if any BAT-AEPL limits are to be developed, a standard for dust emissions measurement should first be developed specifying also that decoking emissions values are to be the average values over the cycle of decoking, and on a wet basis and without oxygen normalization (due to large quantity of steam present for decoking operation and the extremely variable air excess during the decoking process).

Industry position 8: no BAT-AEPL for dust emissions during decoking.

12. BAT-AEPL for CO during decoking.

As mentioned in paragraph 11, decoking should be regarded as other than normal operations
The exact amount of CO formed during the decoking process will depend on the decoking recipe developed by the operator who already has significant incentives to achieve a minimum decoking frequency and time for a maximum runtime. As for dust emissions during decoking, the industry sector therefore judges that the minor amount of CO emissions from the decoking of steam cracker furnaces does not justify a BAT-AEPL

Industry proposition 9: No BAT-AEPL for CO during decoking.

13. Incorporate possibility for an integrated Emission Approach.

An integrated emissions approach for steam crackers would allow for most cost effective emission reductions and management of emissions of integrated furnace configurations designed to achieve higher overall energy efficiency/lower GHG emissions.

Incorporation of such an approach in the LVOC BREF is also consistent with the integrated emission approach in the REF BREF (Commission Implementing Decision 2014/738/EU (2) BAT conclusions 57 and 58).

The technique consists of managing all NOx emissions to air from the steam cracking units in an integrated manner, by implementing and operating the most appropriate combination of BAT across the different units concerned and monitoring the effectiveness thereof, in such a way that the resulting total emissions are equal to or lower than the emissions that would be achieved through a unit-by-unit application of the BAT-AELs as referred to in the LVOC BREF D1, BAT 30 and associated Table 17.4.

The BAT-associated emission levels for NOx emissions to air would then be calculated according to the following formula, where the NOx concentration that would be achieved for that unit is taken from Table 17.4

This BAT-AEL is expressed by the following formula:

$$\frac{\Sigma\left[(\text{flue gas flow rate of the unit concerned}) \times (NO_x \text{ concentration that would be achieved for that unit})\right]}{\Sigma(\text{flue gas flow rate of all units concerned})}$$

In addition, for each new unit included in the integrated emission management system, the BAT-AELs set out in the relevant BAT Conclusions for that new unit remain applicable.

To monitor the BAT for monitoring emissions of NOx under an integrated emission management technique, the following additional monitoring is required above monitoring of individual furnaces:

- a monitoring plan including a description of the processes monitored, a list of the emission sources and source streams (products, waste gases) monitored for each process and a description of the methodology (calculations, measurements) used and the underlying assumptions and associated level of confidence;
- continuous monitoring of the flue-gas flow rates of the units concerned, either through direct measurement or by an equivalent method;
- a data management system for collecting, processing and reporting all monitoring data needed to determine the emissions from the sources covered by the integrated emission management technique.

Industry position 10: As for the REF BREF, incorporate the option for an Integrated Emission Approach as an alternative to LVOC BREF D1 BAT 30 and Table 17.4