Best Available Techniques (BAT) for the mineral oil and gas refineries

Revision of the refinery BAT reference document is now under way

Industrial sites in Europe are required to have an operating permit issued under the national implementation of the IPPC Directive. The permit conditions require that the emissions to air and to water should be consistent with the application of Best Available Techniques. These are recognised technologies or non-technical measures (such as the application of energy efficiency, good housekeeping, etc.) that can be applied, where practical and cost-effective, to minimise an installation's environmental impact.

To provide guidance on BAT, reference documentation has been developed under the direction of the IPPC Bureau in Seville. This now comprises some 33 documents covering different sectors (vertical BREFs) and generic topics (horizontal BREFs).

Under current legislation the BREF documents are guidance documents only. However, the proposal by the European Commission to considerably strengthen the requirements of the IPPC Directive may result, explicitly or implicitly, in these guidance documents having a more legal status.

This promises to be problematic if the BREF documents do not fully reflect all the different situations that may occur across the entire industry. This is especially true for industries, such as refining, where existing plants are often retrofitted with abatement technology and the number of permutations of design, operational conditions, constraints, etc. is very large.

The current revision of the refinery BREF started in September 2008 and is due for completion in 2010. CONCAWE is represented on the technical working group (TWG) that is overseeing the redrafting using recent industry data. As a contribution to the revision CONCAWE has prepared a report, 4/09, *Refining BREF Review—Air Emissions,* that addresses:

- NO_x emissions from combustion;
- emissions from FCC (fluid catalytic cracking) plants;
- amine treatment;
- effectiveness of sulphur recovery plants; and
- effectiveness of vapour recovery units.

The report provides updated information on the possible emission ranges from these units and how these depend on operating environment. It was not feasible to cover all possible installations, so the emission ranges do not necessarily reflect the minimum or maximum emissions possible.

In this article we look at the work done by a CONCAWE task force when preparing information for the review of the refinery Best Available Techniques (BAT) reference document (BREF). The article focuses on two aspects: NO_x from combustion systems and the effectiveness of sulphur recovery plants.

NO_x emissions from combustion systems

The most used technique for controlling combustion NO_x in refineries is the low NO_x burner (LNB). It is a retrofitted or existing heater application and may be able to fire both oil and gas (dual fired) or gas only. There are different types of burner design and the unique characteristic of refinery applications is that, because internally generated fuels are used, the fuel composition may vary considerably over time. Similarly, operating conditions may be different from unit to unit. Such differences can have a strong effect on NO_x, as can measures to improve overall energy efficiency, such as preheating the combustion air.

These sensitivities raise the question of what is an appropriate range of NO_x emissions for a low NO_x burner, as the permit authorities need to judge emission performance relative to 'typical values' for the technology expressed as a range of BAT AELVs.

Figure 1 NO_x for staged-air LNB firing refinery fuel gas

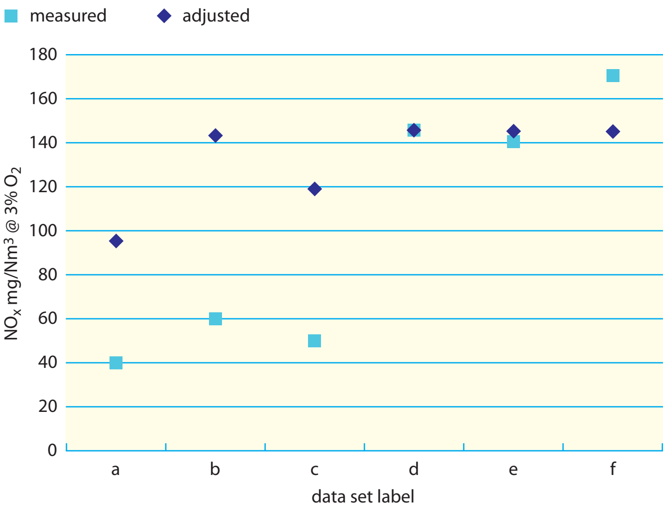
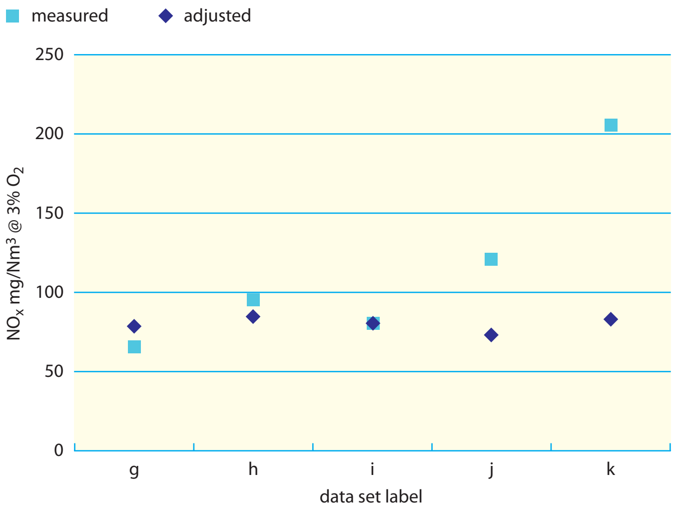


Figure 2 NO_x for staged-fuel LNB firing refinery fuel gas



Figures 1 and 2 show NO_x emissions from a total of 11 installations, each having different operating conditions. The installations in Figure 1 use 'Staged-Air Low NO_x Burner' technology; those in Figure 2 use 'Staged-Fuel Low NO_x Burner' technology.

The squares show the measured NO_x concentration. The diamonds indicate the 'intrinsic' performance of each technology for CONCAWE's standardised conditions. The difference between the diamonds and the squares is the variation in NO_x due to the operating conditions.

The CONCAWE report compares several sets of real plant data, taking examples across a wide number of different applications. The variability in NO_x across these applications is examined using correlations from the Dutch regulations[1] to see if this enables the underlying 'technology' contribution to NO_x emissions to be discerned.

Figures 1 and 2 show the effect of operating conditions on NO_x emissions calculated for two burner types burning refinery fuel gases. The first is a staged-air low NO_x burner; the second is a staged-fuel low NO_x burner. The squares are the measured data. The diamonds show the data converted to a single standard set of standardised operating conditions. The main corrections are for fuel hydrogen content, air preheat temperature and firebox temperature.

It can be seen that, although measurements on individual installations appear very different, these differences are consistent with the specific local conditions. The underlying control technology, 'the low NO_x burner', has essentially the same standardised emission in each of the cases considered—noting of course that there are different types of low NO_x burner.

Although the figures only show results for gas firing using staged-air and staged-fuel burners, CONCAWE report 4/09 also includes results for dual fired burners and ultra-low NO_x burner types.

Having established that the low NO_x burner may have different emissions according to operational needs, the report suggests how associated emission ranges might be derived that fairly describe the local application. Important considerations are, for example, the use of air preheat to increase efficiency, which is highly desirable to reduce CO_2 emissions but has a penalty on NO_x. A change in fuel hydrogen content might occur during normal operation, and this also has implications for NO_x.

Sulphur recovery efficiency

Sulphur recovery is a very important part of refining operations and key to overall control of sulphur emissions. For the purpose of providing data for the BREF

[1] *Ministerie van VROM (1987) Besluit emissie-eisen stookinstallaties milieubeheer A (Bees A). Staatsblad van het Koninkrijk der Nederlanden Stb. 164, 1987.*

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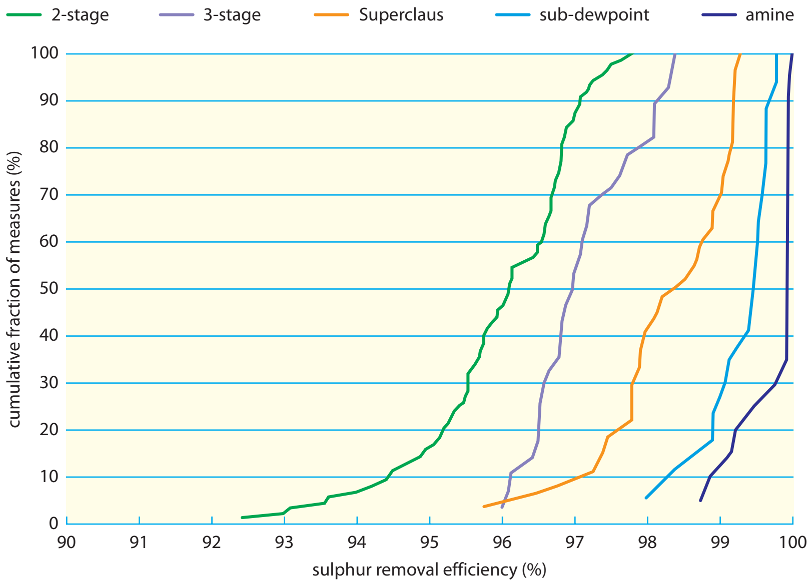
Figure 3 Sulphur removal efficiency



Overall sulphur efficiency for the stages in a sulphur recovery process. Generally, units comprise a 2- or 3-stage Claus unit followed by a Superclaus process or a sub-dewpoint process, or an amine treatment process.

review CONCAWE contracted a consultancy firm, Sulphur Experts, to produce a review of European sulphur recovery units' (SRU) efficiency. The results are derived from a database of measurements made by Sulphur Experts as part of their work in advising refineries on their SRU operations. The database includes both refineries and gas plant applications, but only European refinery data is described here.

The inspection of SRU performance includes measurements on each stage of the process. The database therefore allows the recovery efficiency of the individual stages of the sulphur recovery process to be assessed. The assessment excludes any proportion of sulphur that passes to the final stage incinerator either directly in supplemental fuel or from degassing of the sulphur product, so real-life sulphur capture may be less than the technology indicates is possible by a small amount.

A sulphur recovery unit typically comprises a 2- or 3-stage Claus unit followed by a tail gas unit. There are a number of different tail gas processes based on different technologies. Figure 3 shows the cumulative distribution of measurements of sulphur capture efficiency taken after each stage in the recovery process.

The categories were 2-stage Claus unit, 3-stage Claus unit followed by tail gas treatments: oxidative (Superclaus), sub-dewpoint (variants not distinguished) and amine treatment.

The overall efficiency at the treatment stage is shown so, for example, the Superclaus curve comprises measures made on units having a 2- or 3-stage Claus unit followed by the Superclaus treatment.

As illustrated in Figure 3, there is a distribution of observed efficiencies across the measurements taken. The 100% percentile corresponds well to the manufacturers maximum efficiency for the technique. The median efficiency observed for the 2-stage Claus was 96.1% increasing to 97% for the 3-stage and 98.5% for the Superclaus. Sub-dewpoint technology tail gas units increase this to 99.5% and amine scrubbing is the only technology that achieves efficiencies above 99.9%. The information in the current BREF relating to daily average performance is shown in Table 1.

In terms of BAT choices this is very important, as setting capture efficiency targets above 99.7% essentially requires the installation of amine treatment.

These results on the different components can be compared with a crude estimate of recovery efficiency obtained from the regular CONCAWE survey of refinery sulphur emissions. These efficiencies are derived from the annual sulphur balance using the amount of recov-

Table 1 Daily average performance data (from current BREF)

	Process	Expected daily average sulphur yield (%)
Claus unit	Claus 2-stage	94–96
	Claus 3-stage	97–98
Tail gas clean-up units	Superclaus	98.66
	Sulfreen	99.42
	Beavon	99–99.9
	CBA	99–99.50
	Clauspol	99.5–99.9
	Clauspol II	99.60
	SO_2 abatement	99.9
	Hydrosulfreen	99.67
	Doxosulfreen	99.98
	RAR	99.94
	LO-CAT II	99.99
	SCOT	99.5–99.99

ered sulphur and the estimated sulphur feed to the SRU. The data may include periods of non-ideal operation.

Figure 4 shows the distribution of sulphur recovered in years 1998 and 2006, overlaid upon Figure 3. Year 2002 is not shown due to the limited data set, although we can comment that the top quartile results (distribution with recovery > 99%) were similar.

The Sulphur Experts database reported 127 investigations on 2- and 3-stage Claus units and 62 on tail gas units of which 26 were Superclaus, 17 were sub-dew point and 19 were amine treatment plants. If one were to assume no duplicate measurements and that measurements were always made across all installed units, then this would give 51% without tail-gas units, 20% with Superclaus units, 13% using sub-dewpoint technologies and 15% with amine treatment.

This split is not inconsistent with the 2006 survey results which would indicate perhaps up to 30%, rather than 20% usage of Superclaus technology, 10% using sub-dewpoint technologies and 10% using amine treatment.

The trend with time suggests a definite improvement in sulphur recovery efficiency. The largest change occurs for those reporting capture efficiencies between 97% and 99% and would be consistent with improved operation of (or investment in) 3-stage Claus plant and investment in Superclaus technology. Median recovery efficiency increased from ~97.4 to ~98.3%.

This picture suggests that the choice of recovery efficiency accorded to BAT could have major implications for European refining. Any recent investment in Superclaus (or Euroclaus) technology could be insufficient if capture efficiencies of 98% were to be excluded from the BAT AEL ranges. CONCAWE therefore proposes that the BAT AEL range for existing plant should be 98–99.9% and for new facilities 99–99.9%.

Taking the NO_x and sulphur recovery results together illustrates some fundamental facts:

Figure 4 Sulphur removal efficiency (from the CONCAWE sulphur surveys)

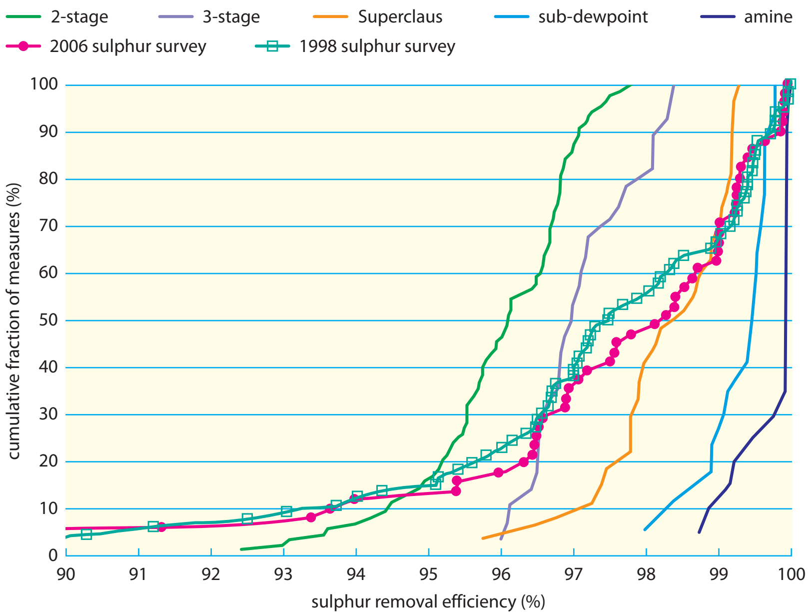


Figure 4 Estimated annual sulphur capture efficiencies from the CONCAWE 1998 and 2006 sulphur surveys overlaid on the Sulphur Experts unit-specific data.

- The industry is very diverse with many different types of installation within any broad category such as low NO_x burner or sulphur recovery plant.
- Operational data is needed to establish the realistic performance range and how this varies between installations, taking full account of retrofit possibilities and constraints.
- The effect of operating variables and co-effects needs to be recognised. For example, air preheat to increase efficiency will raise NO_x.

CONCAWE will continue to inform the debate with factual data contributed by its members.