CONCAWE sulphur survey

Tracking the fate of sulphur through the refining process

Since 1979 CONCAWE has conducted a regular four-yearly survey of its member companies to determine how the fate of sulphur through the refining process changes over time. The last sulphur survey was for the year ending 2006. The main results are presented below.

Sulphur is an intrinsic component of all crude oils and is generally undesirable in those oil products destined for combustion because of the potential environmental impact of SO_2 emissions and/or poisoning of catalytic exhaust gas clean-up systems. Over time, there has been, therefore, a constant focus on reducing both the sulphur content of commercial fuel oils and emissions from the refining process itself, which makes use of its internal streams for a large portion of its energy needs. In recent years, sulphur has all but been eliminated from road transport fuels, not because of the potentially harmful effects of sulphur, but to enable the use of exhaust after-treatment technologies for the abatement of regulated pollutants such as NO_x, carbon monoxide and particulate matter.

Table 1 shows the change in the distribution of sulphur amongst the different compartments since 1998. The proportion of sulphur in oil products sold for fuels has decreased from 37.0 to 32.5% of the total sulphur intake. An even lower figure was derived from the 2002 survey, although we believe that this was due to under-representation of refineries supplying the heavy fuel oil markets, as discussed later in this article. The proportion removed from the various refinery streams and recovered as elemental sulphur reached 45% in 2006 and is now the largest sulphur stream. The proportion of sulphur emitted directly to the atmosphere from refineries reduced to 3.7% of the total input in 2006, from about twice that figure in 1998.

Table 1 Overall balance of sulphur from 1998–2006

% sulphur intake		1998	2002	2006
Output	Products for combustion	37.0	29.8	32.5
	Products not for combustion	14.5	8.6	11.8
	Recovered as elemental sulphur	39.4	47.6	45.0
	Recovered as other compounds	1.4	5.5	0.2
Emitted at refinery	All sources	7.2	5.5	3.7
Balance		**99.5**	**97.0**	**93.2**

A trend towards less liquid refinery fuel and with a lower sulphur content

The reduction in sulphur emissions from refineries has come largely from combustion installations as is shown in Table 2, and this has been achieved in two ways—a reduction in the sulphur content of the internal fuel oil used in refineries and a greater penetration of gas firing from both internally generated gas and purchased natural gas. In 2006 refineries accounting for almost 20% of combustion energy use were gas fired (see Figure 1). Only a very small amount of pure oil firing remains in 2006, typically in specialist bitumen refineries. In most EU refineries today, liquid fuels account for less than 50% of the total fuel burnt.

Refinery SO_x emissions can be regulated under the 'bubble' concept

The Large Combustion Plant Directive (LCPD) of October 2001 gives refineries the option to adopt a combustion 'bubble' representing the average stack concentration

Table 2 Distribution of refinery sulphur emissions from combustion

Emissions (% sulphur intake)	1998	2002	2006
Stacks	4.6	3.1	1.8
FCCU	0.4	0.2	0.4
SRU	0.8	1.3	0.6
Flares	1.0	0.6	0.8
Miscellaneous	0.4	0.2	0.2
Totals from all sources	**7.2**	**5.5**	**3.7**

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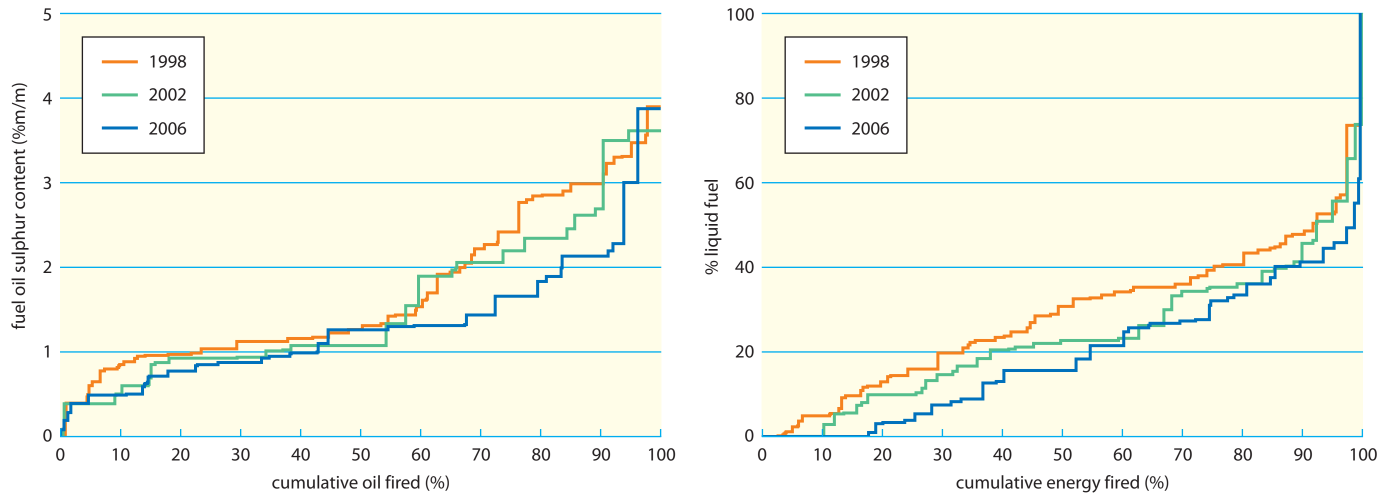
Figure 1 Distribution of refinery fuel oil sulphur content and fraction of fuel oil burned

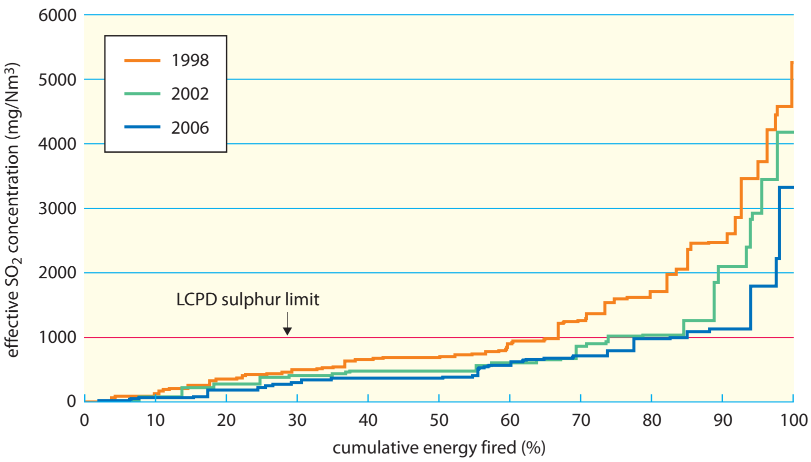


over all large combustion installations on the site (defined as having a design firing rate exceeding 50 MW thermal). The evolution of the combustion bubble over the period 1998–2006 is shown in Figure 2. In 1998 refineries representing about 60% of energy fired had a bubble concentration below the LCPD limit of 1000 mg/m^3 SO_2. In 2006 that had increased to nearly 90%. The latest date for implementation of the LCPD was 1 January 2008 so we might expect to see further reductions in the bubble concentration in the next survey.

The results shown so far reflect the cumulative results over all of Europe, whereas there are locations where emission regulation is tighter to reflect the higher environmental sensitivity to acid gas emissions. The evolution of the LCP bubble on a regional basis is shown in Figure 3 where the horizontal axis is now the cumulative energy fired in each region. In 1998 refineries in the Mediterranean area and in Spain (marked ME), and Northern France and the UK (marked AT) had much greater SO_2 LCP bubble values than those in the Benelux and Northern and Central Europe (marked NW). By 2006, the gap had very much closed even though the trend for continued reductions in the NW area is evident. The group labelled OT is the LCP bubble for other refineries in the survey. The geographic location covered by this group is different in 1998 and 2006, so these results are not directly comparable.

Figure 2 Large combustion plant bubble (plants over 50 MW)

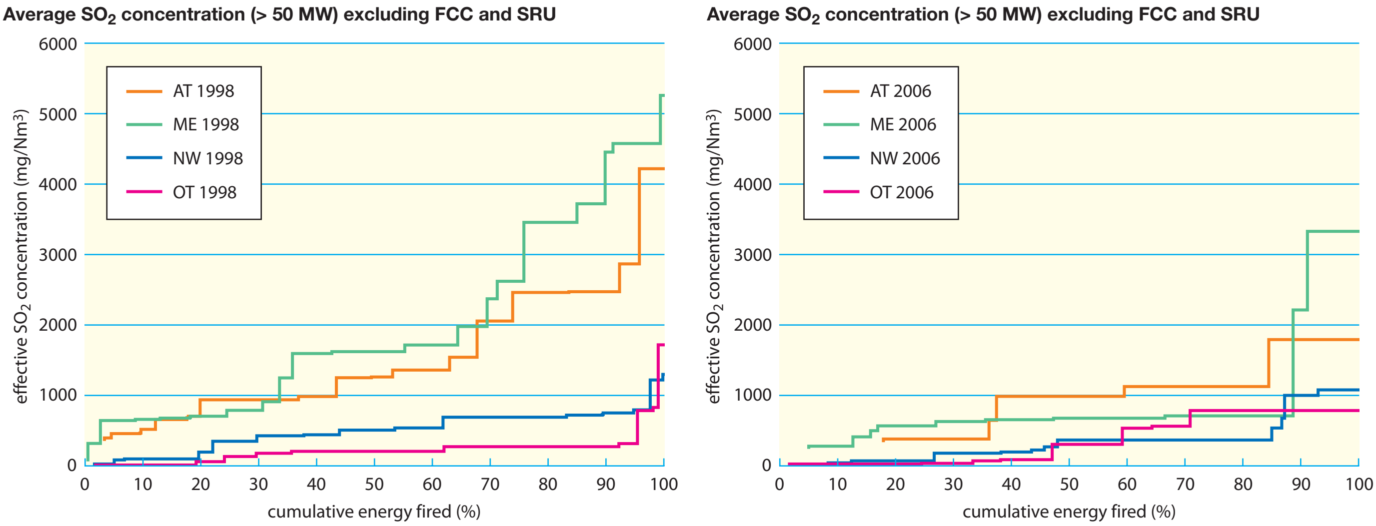
Average SO_2 concentration (> 50 MW) excluding FCC and SRU



We have seen that, overall, the sulphur content in oil products for combustion has decreased over the period. This is mainly the result of legislated changes in the maximum sulphur content of road fuels, gasoils and inland heavy fuel oils.

One area for further sulphur reductions is the marine fuels market. The sulphur content of marine fuels is regulated on a worldwide basis through the International Maritime Organization (IMO). An agreement under the International Convention for the Prevention of Pollution from Ships (MARPOL), known as MARPOL Annex VI, introduced a global sulphur content cap of 4.5% m/m as of May 2005. It also introduced the

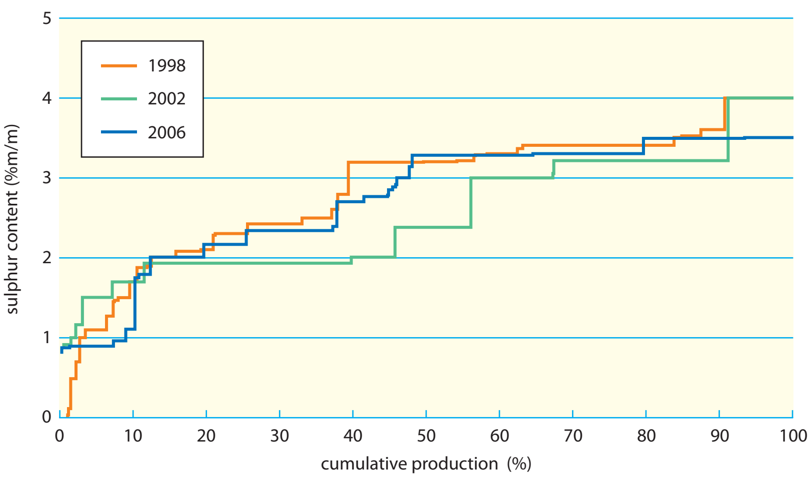
Figure 3 Evolution of the LCP bubble by region, 1998–2006 (plants over 50 MW)



concept of Sulphur Emission Control Areas (SECAs) which are special sea areas where ship sulphur emissions must be consistent with a fuel having a maximum sulphur content of 1.5% m/m. Following its ratification in 2005, MARPOL Annex VI came into force in May 2006 for the Baltic Sea and November 2007 for the North Sea. In addition, the EU adopted Directive 2005/33/EC which extends the 1.5% m/m sulphur limit to 'passenger ships on a regular service to or from an EU port' (further referred to as 'ferries') and which came into effect in August 2006. The Directive includes a review clause whereby the possibility can be envisaged for the extension of the sulphur limit to all EU waters, and to its further reduction. The IMO recently adopted a proposal to decrease the maximum sulphur content in SECAs to 1.0% by 2010 and 0.1% by 2015, and to decrease the global marine fuels sulphur cap to 3.5% by 2010 and to 0.5% by 2020 or 2025 at the latest (subject to a review in 2018).

Figure 4 shows that the distribution of marine fuel sulphur content was virtually identical in 1998 and 2006. The 2002 survey results appear to have under-represented the number of refineries that produce marine fuel oil, as can be seen by the smaller number of steps in the curve, and this is probably also the reason for the anomalous trend observed in Table 1.

Figure 4 Sulphur content of marine fuels, 1998–2006



This article has described some aspects of the 2006 sulphur survey, the full results of which will shortly be published as a CONCAWE report. Emission regulations have successfully driven refinery emissions down, slowly eliminating geographic variations. As the limits on the maximum sulphur content of refinery products have been tightened, sulphur recovered as elemental sulphur from the desulphurisation of refinery streams has increased and is now the biggest endpoint for sulphur in crude. The sulphur content of marine fuels, which shows no change in the period 1998–2006, is now entering a period of change which will no doubt be reflected in the 2010 survey.