

## PCDD/F EMISSIONS FROM LUBRICATING OIL COMBUSTION – REDUCED EMISSIONS WITH INCREASE IN CHLORINE

Dyke P H<sup>1</sup>

<sup>1</sup>PD Consulting, Hereford, UK

### Abstract

The test programme described in this paper was carried out to find the effect of changes in levels of chlorine in lubricating oil on emissions of PCDD/F when the oils were burned in relatively simple, commercially available combustion equipment with no pollution controls.

Nine tests were conducted using three lubricating oils formulated using only base oils and additives that are used for commercial lubricants. The three levels of chlorine were achieved by using two different dispersants. Tests were conducted on a commercial waste oil-burning unit operated at steady state conditions for periods of 6 hours.

The results show that emissions of PCDD/F *decreased* with increasing chlorine. The effect was clear and unambiguous for these tests and these oil formulations. Further work is underway to investigate this phenomenon further.

### Introduction

This programme of testing was initiated in order to find out whether changes in the formulation of lubricating oils, primarily changes to the dispersant used and hence the levels of chlorine in the oils, affected emissions of PCDD/F from waste oil combustion. In many countries a significant proportion of used or waste oils are either burned as received or burned for fuel after relatively little processing. The combustion systems used vary from very simple burners providing space heating in garage and workshop premises through to cement kilns, power stations and other regulated, well-controlled, large-scale systems.

Lubricating oils used for cars and trucks often makes up a substantial proportion of the used oils in a country. However, it is important to note that mixed waste oil streams may contain components that are quite different to lubricating oils – such as cutting oils and solvents – which can increase levels of chlorine for example.

Modern lubricating oils are carefully formulated using a package of additives to meet stringent performance criteria and serve multiple purposes – the main ones being to provide effective lubrication and maintain cleanliness in the engine over the full period between oil drains.

A key component of the additive package is the dispersant. This acts to keep dirt in suspension and thereby avoids the build up of potentially harmful deposits in the engine. There are two main routes to produce dispersant chemicals for lubricating oils – “conventional” and “DA” - direct alkylation or “thermal” (due to higher energy consumption). The conventional route involves the use of chlorine as a catalyst, the DA process achieves the reaction using thermal energy. Oils formulated with conventional dispersant would typically have residual chlorine levels of up to 150ppm while those using DA dispersant would have up to 20ppm chlorine from components other than the dispersant.

Some regulators and oil specifiers have sought to drive a move to lower chlorine lubricating oils. The assumption has been that lower chlorine must be “better” environmentally and that lower chlorine would lead to lower PCDF/F.

Considerable work has been done to reduce the amounts of chlorine in dispersant and hence the finished lubricating oils but removal is not straightforward and increases the energy consumption. In order to understand the environmental balances thrown up by this trade-off between increased energy consumption and

lower chlorine for conventional dispersant and the choice of changing to DA dispersant, Lubrizol adopted a life-cycle assessment approach.

Over the past few years Lubrizol have undertaken extensive studies of the life-cycle for engine oils with a particular focus on the impacts of different choices of dispersant. The life-cycle impacts are dominated by the use-phase – which is to be expected since the greatest amounts of fuel and materials are associated with the vehicle use rather than lubricant production or disposal. These studies have shown that, to achieve similar performance, greater quantities of DA dispersant are required compared to conventional leading to increased energy consumption and associated environmental impacts in production. In addition, the frictional properties of the dispersants are subtly different which is the most significant difference between them. Using DA dispersant instead of conventional can lead to an increase in fuel consumption in the vehicle by downgrading the frictional properties of the lubricant.

Since the issue of PCDD/F is controversial and there are inconclusive data on the effect of small changes to the level of chlorine in lubricating oil on emissions from engines, Lubrizol undertook a detailed experimental programme designed to find out if the change in chlorine in lubricating oil caused by choice of dispersant would yield a change in emissions of PCDD/F from engines. This work, involving 40 sampling runs, has been reported at Dioxin 2005<sup>1</sup>, Dioxin 2006<sup>2</sup> and in Chemosphere<sup>3</sup> and showed that the chlorine flow in the engine was dominated by the chlorine in the fuel (albeit at very low levels), that PCDD/F emissions were not increased by increases in chlorine in oil or fuel and that levels of PCDD/F were low. In addition the work demonstrated for the first time that the use of a diesel oxidation catalyst in the exhaust reduced emissions of PCDD/F to about a fifth of their levels with the catalyst removed.

In order to provide measured data on the effect of a change in chlorine in the lubricating oil during the disposal phase of the life-cycle we organized a programme of tests which began in spring 2007 and should be completed by autumn 2007.

### Materials and Methods

For these tests we established the following principles:

- Tests should be on commercially available combustion equipment;
- Repeated tests were required at each condition since emissions tend to be variable;
- Steady state conditions should be used to ensure repeatability;
- No artificial doping would be used to control chlorine content – ie the oils would only have components found in real lubricating oils;
- Three test oils would be used (as for the engine tests) with a range of chlorine related to the choice of dispersant.

A waste oil fired air heater was purchased (Thermobile AT400). The unit was one of the smaller ones available with an output of 41kW and operates on a relatively simple principle with the oil being fed onto a pan and burned. This was designed to be representative of units that are being sold in the UK and elsewhere in Europe now and being installed in a garages and workshops.

Oil from a tank is pumped into the combustion chamber and from the fuel supply pipe onto a cast iron dish where it vapourizes and is burned with input air from the single forced draught fan. Combustion gases from the cylindrical combustion chamber pass through an air-air heat exchanger and into the flue. In our tests we had a stainless steel flue (supplied with the burner) rising vertically a distance of approximately 6m. The stack was fitted with sample points to facilitate extractive sampling using modified method 23 equipment for PCDD/F. In addition combustion gases were extracted and analyzed continuously for CO, CO<sub>2</sub>, SO<sub>x</sub>, NO<sub>x</sub>, and volatile organic compounds (VOC). Temperatures in the lower stack were measured.

For each run the boiler was lit using paper and 300ml of diesel in the burner dish (as per the instructions) and the

unit run for 20 minutes on low fire. Then the unit was switched to high fire and run for 2 hours and monitored to ensure steady conditions were being achieved. After the two hour conditioning run sampling was commenced for PCDD/F. Sampling was by conventional filter – condenser methods, the sample probe was titanium. The principles of EN1948 were followed. Isokinetic sampling was not possible due to the low stack velocities inherent in this type of equipment. Levels of particulate were low and it is not thought that deviation from isokinetic conditions will have affected the samples. A target volume of 10 m<sup>3</sup> of sample was set and this was achieved in about 6 hours.

At the end of the test the unit was allowed to cool, any remaining oil was drained and the tank cleaned. The burner pan, fuel feed pipe and combustion stabilizer were cleaned of any soot or other deposits with wire brushes and a vacuum cleaner.

An initial series of nine runs was planned and reported here. Three runs for each of the three oils were conducted.

### Results and Discussion

The unit was installed and commissioned using diesel as fuel. Stable conditions were achieved. For the nine test runs the temperature in the base of the flue was around 290 °C. Combustion was highly effective operating the unit with no intervention during the test periods, levels of carbon monoxide and VOC were low. In one run (test 4) there appears to have been a build up of residue in the burner pan that affected the fuel supply pipe and caused short-term spikes in VOC and CO levels.

In each test there was some build up of residue in the burner pan. This had a mixed nature with some sooty/char components (possibly arising during final burnout), residue of the paper used to light and mineral matter that came from the oil. There was little sooting in the combustion chamber but some sooty deposits on the burner stabilizer.

Test number	Oil chlorine content	PCDD/F ng I-TEQ Nm <sup>-3</sup> @ 11 % O <sub>2</sub> (dry)	Emission factor pg I-TEQ l <sup>-1</sup> of oil
1	131	0.00073	12.71
2	12	0.00069	13.54
3	259	0.00056	11.06
4	259	0.00027	5.21
5	12	0.00091	17.93
6	131	0.00049	9.52
7	12	0.0012	22.79
8	259	0.00032	6.32
9	131	0.00077	15.04

ND – set to zero

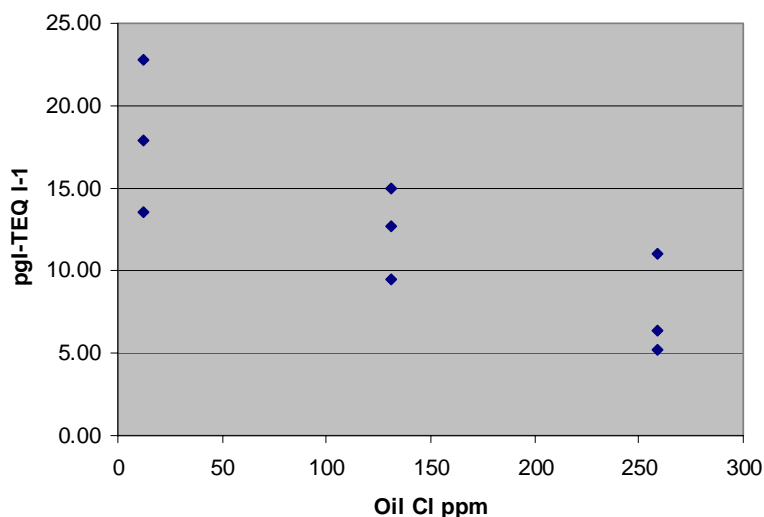
**Table 1 Summary results – PCDD/F emissions**

Emissions concentrations of PCDD/F (summarized in Table 1) were low in the range 0.3 to 1.2 pg I-TEQ Nm<sup>-3</sup> (dry gas 11% O<sub>2</sub>) which can be compared to the widely used emission limit of 0.1 ng I-TEQ Nm<sup>-3</sup>. This translates to emission factors of 5 to 23 pg per litre of oil.

These results are presented graphically in Figure 1 showing emission factors plotted against oil-chlorine content. Visual inspection of these initial results shows that there appears to be a repeatable relationship between oil chlorine content and PCDD/F emission. While releases are low in every case, in these tests, there was a clear

and apparently linear trend to *lower* emissions with increasing chlorine content.

The pattern of congeners and homologues for these tests has been examined and no important differences between the different oils were apparent. In the previous engine test work we had identified a very characteristic pattern that showed high TCDF and that the vast majority of the TCDF was 1,3,6,8 TCDF in the tests where the engine was fitted with a diesel oxidation catalyst, without the catalyst the pattern reverted to a more conventional mixed combustion pattern. No unusual pattern has been observed in these tests.



**Figure 1 Emission factors and oil-chlorine content**

At this stage it is not possible to provide an explanation for why the emissions in these tests are reduced with the oils containing higher levels of chlorine or whether that finding will be observed in further testing. These data show that the emission of PCDD/F from the combustion of these lubricating oils in readily available combustion equipment (with no pollution controls) does not increase with increasing chlorine content arising from the dispersant. In fact a clear trend to lower emissions with increasing chlorine is observed. Further testing is planned to examine emissions from used oils and to investigate this phenomenon of reduced emissions with the higher chlorine dispersant.

### Acknowledgements

The author would like to thank Lubrizol for supporting this work, and providing the test oils, in particular Terry Thiele, Mike Sutton and Barry Hemans. Sampling was conducted by Alcontrol Ltd and particular thanks are due to Sam Thorneycroft. Analysis was by SAL and the contribution of David Wood is acknowledged. The combustion unit was operated at Gastec at CRE by Lesley Thomas and Andy Pittaway.

### References

1. Dyke PH, Sutton M. *Organohalogen Comp* 2005, 67
2. Dyke PH, Sutton M, Thiele T, Collins M. *Organohalogen Comp* 2006, 68
3. Dyke PH, Sutton M, Wood D, Marshall J. *Chemosphere* 2007, 67: 1275