

## OBJECTIVES

The objectives of this project were;

- To demonstrate that on-line Polycyclic Aromatic Hydrocarbon (PAH) concentration measurements can be used as quantitative indicators of utility boiler efficiency.
- To establish the methodology for using PAH detecting instruments to track changes in boiler efficiency and the combustion environment to enable better boiler management.

This being achieved through;

- Identification of a candidate instrument for measurement of PAH on-line and modify, if necessary, for use in pulverised coal-fired boiler gas ducts.
- The generation of PAH "tracers" under controlled combustion conditions at pilot scale.
- To build-up data set of PAH signatures as a function of combustion efficiency and boiler combustion conditions at pilot scale.
- To conduct a full-scale boiler test series to supplement pilot scale data.
- Development of methodology relating PAH signatures to efficiency and combustion conditions, leading to prototype system.

## SUMMARY

A literature survey was undertaken on the application of measurements of PAH from power plants as an indicator of combustion performance. In the publications considered it is generally found that there is a correlation of PAH with Carbon

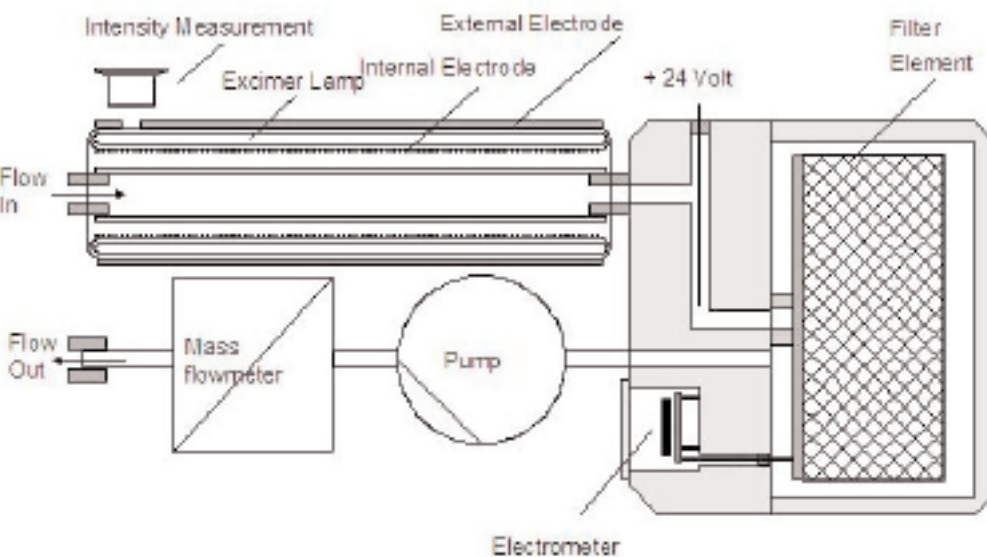


Figure 1. PAS 2000 Process Schematic

Monoxide (CO) or other equivalent measure of incomplete combustion. However the absolute value of the ratio of PAH/CO or other measure of incomplete combustion changes from plant to plant, and depends on the plant design and the air pollution control equipment in place.

The PAS2000, which uses a photoelectric aerosol sensor, was considered a potentially suitable monitor due to its ability to make online measurements and the importance of the sample conditioning was noted. A process schematic of this instrument is shown in Figure 1. A significant amount of effort was directed towards optimising the sampling system.

In the first instance this involved the inclusion of a dilution probe with the intention of diluting the gas stream prior to the analyser, to ensure its protection. However, the levels of PAH encountered in the pilot scale rig were found to be lower than expected and the dilution probe was not used. Problems were then experienced with blockages within the analyser. This meant that in order to apply the analyser to full scale a new design of sampling system was needed.

Following the pilot scale trials a new system was developed, based upon a dichotomous sampler and utilising a venturi needle to extract a side sample of smaller particles, at a much lower flow rate than the main sample, to supply the PAS2000. However, the system did not work as well as it was hoped and the analyser was

rendered useless by the components of the flue gasses.

It was concluded that although the only equipment that is currently commercially available worked well enough at pilot scale, it was simply not robust enough for application at full scale.

## BACKGROUND

Pulverised coal-fired utility plant is under increasing pressure to operate at the highest possible efficiency, while remaining within the limits set by regulatory bodies on environmental pollutants. Because fuel costs are the single largest factor in power station operations, even small savings made here are highly desirable in real terms. It is for this reason that utility companies worldwide are investing in control strategies that maximise the efficiency of boiler operation through the control of important boiler variables in, or as near to, real-time as possible. In the UK, the recent introduction of Integrated Pollution Prevention and Control (IPPC) mandates plant operators to operate at the highest practicable efficiency, and this provides an additional impetus to achieve improvements to operating practice that result in efficiency gains.

For the best control over boiler operation, it is necessary to utilise easily measured boiler parameters that respond quickly to changes in the combustion environment. This is normally achieved through continuous monitoring of excess oxygen and carbon monoxide concentrations. An additional and valuable measurement of boiler combustion efficiency is the carbon-in-fly-ash concentration. However, this requires an extractive sampling technique, and even the latest generation of carbon-in-ash analysers operates on a semi-batch basis, and so cannot give real-time data.

An on-line technique that is robust, relatively simple to operate and maintain is likely to be of particular value to the new generation of intelligent control systems aimed at minimising emissions of pollutants such as NO<sub>x</sub>. The development of a real-time combustion efficiency analyser is the focus of this project.

The combustion products that have been selected as the basis of the current research are Polycyclic Aromatic Hydrocarbons (PAHs). PAH are thought to be produced, in systems firing fuels such as coal, by three basic mechanisms:

- Incomplete pyrolysis of fuel molecules generating single or multiple-ring fragments.
- The joining of small ring systems released during combustion to form larger polycyclic systems.
- The cyclisation of linear carbon chains to form PAHs.

Clearly these mechanisms are not exclusive and it is highly likely that all will operate to a degree in a given environment.

## **EXPERIMENTAL RESULTS**

Almost all measurements of PAH are made by sampling onto suitable media followed by

recovery and concentration before analysis using such techniques as Gas Chromatography/ Mass Spectrometry (GC/MS) or Liquid Chromatography/ Fluorescence (LC/F). The only commercially available instrument that was identified as able to make on-line measurements of PAH in real-time is the PAS2000 system, which is aimed at the ambient air quality sector and is marketed by EcoChem.

In order to use this analyser in a combustion environment it was essential that a suitable sampling system be developed to prevent overloading/blocking of the system with excessive levels of particulates. The sample conditioning system developed consists of a heated probe and a dilution system.

During the pilot scale trials it was discovered that the levels of PAH generated in the CTF were lower than expected and consequently the dilution facility on the sampling probe was not used, indeed use of the dilution facility would have significantly reduced the level of detection achieved. The PAS2000 is intended to be suitable for high particulate load environments through the use of the dilution probe. Without the use of the dilution facility the instrument is much more susceptible to blocking due to the design of the filter and the electrode housing, as was discovered during the pilot scale trials. For this reason it was clear that a new sampling system had to be devised in order to apply the system to a full scale boiler.

A sample probe was built which allowed an extractive sample to be taken, from which a side sample was removed and passed through the PAS2000. The whole probe assembly was heated, to avoid condensation of the moisture content of the flue gas within the sample lines. A cyclone and catchpot were included in the main sample line, to protect the pump from the particulates and moisture within the gas. It was not possible to use these items in the side sample, as the analyser requires a flow

of particulates in order to detect the PAH molecules. The belief was, however, that these items would not be necessary due to the significantly lower flow rate going through the side sample, compared to the flow through the main sample line. The intention was that the majority of the larger particles and moisture would remain entrained in the main sample line, while the venturi needle would extract only the smaller particles through its reverse suction and thereby limit the potential for damage to the analyser. A diagram of this sample system is shown in Figure 2.

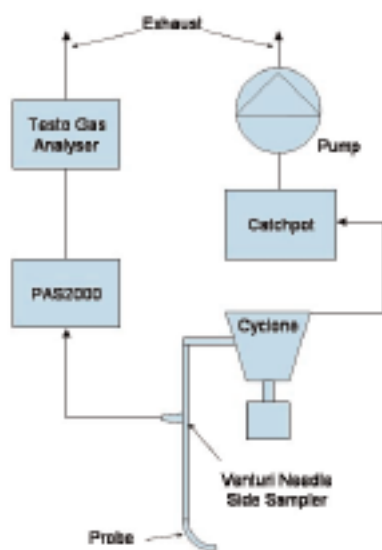


Figure 2. Schematic of New Sampling System

The relationship between compositions of flue gas from the pilot scale rig and levels of unburned material in fly ash collected simultaneously were evaluated. The relationship for the rig will not be the same as for full-scale plant due to the effects of scale on temperature profiles, mixing and residence time. However, relationships between the measured parameters are expected to be of the same form. These relationships were investigated for three coals Daw Mill, Thoresby and El Cerrejon. They were found to be of a similar form for all three coals. The relationship between Oxygen concentration and level of unburned material in the flyash was found to be an inverse exponential one.

The results suggest that the size (thermal rating, residence time) of the combustor does not allow good mixing because the CO concentrations and Unburned Carbon (UBC) in ash are higher than those commonly observed in a large power station. However the results are generally consistent with the relationship between CO concentration (combustion efficiency) and the PAH concentration, and this is in turn consistent with the observations made earlier where this relationship holds for a number of systems irrespective of the level of incomplete combustion as long as the combustion temperature is approximately the same.

The PAH results consist of a series experimental measurements with filters with different pore sizes in the sampling train (0.8, 8, 63 m pore size) and also with a cyclone only. The difference in the use of these filters is that they will influence the ratio of gaseous to solid phase PAH but should not influence the total amount of gaseous PAH. It is presumed that the detector only sees particulate PAH condensed onto the carbon substrate and part of the gaseous PAH that is adsorbed onto the carbon particles, but all of these processes are determined by temperature. The filters will also influence the particulate material that is sampled; thus the cyclone will permit the passage of the fly ash, the unburned carbon-in-the-ash and any soot present. Only the unburned carbon in ash (and soot) will be active and the fly ash will not produce a photoelectric signal, its only role will be to absorb gas phase PAH. It is not expected that this absorbed PAH will give a signal unless the surface is conducting.

The results with the 0.8 m filter showed some agreement with the concept of PAH and CO proportionality. Although some PAH appears to be detected without CO occasionally, this could arise from the small size of the combustor and the total lack of

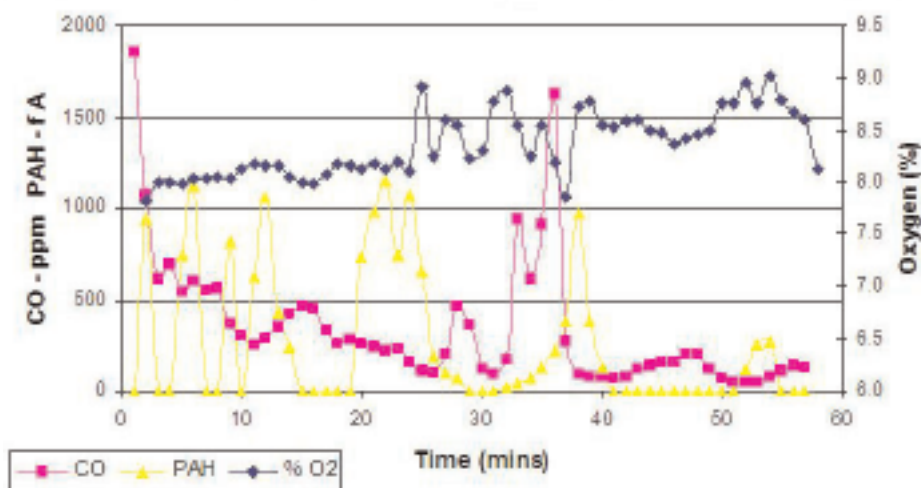


Figure 2. CO and PAH Trace

mixing for some of the devolatilising coal particles. It should be noted that the small filter pore size would probably mean that the particulate PAH will not penetrate but this depends critically on the temperature of the filter, and it also means that much of the unburned carbon will not be in the detection zone (only soot). As far as the results from the coarser filters, 8 m and 63 m, are concerned the relationship between the PAH and CO does not seem to hold. This probably results from the fact that fly ash now passes into the detection zone absorbing much of the PAH.

The full scale trials were not without incident, but eventually some reliable data sets were collected. However, the data did not show the anticipated trends.

Figure 2 shows a typical trace of carbon monoxide, oxygen and PAH measurements from Unit 2 at Ironbridge. It can clearly be seen that while the CO and O<sub>2</sub> respond to changes in the combustion environment in the anticipated manner, the PAH readings are much more erratic. Figure 3 shows the comparison between NO, SO<sub>2</sub> and PAH.

At the time of sampling the coal feed rate was slowing for reasons beyond our control, this explains the gradual decline in SO<sub>2</sub> and as the combustion air flow was not being reduced as quickly, the NO level was showing an associated increase. The PAH levels however, do not illustrate any distinguishable pattern which can be tied to the conditions in the boiler at the time of sampling.

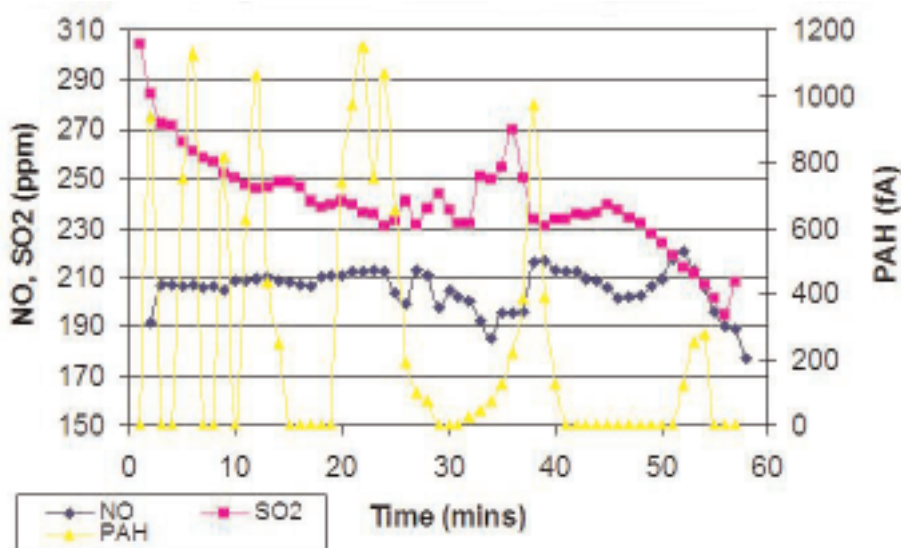


Figure 3. NO, SO<sub>2</sub> and PAH Trace

After only a few hours of sampling the PAS2000 returned an electronic error message which could not be cleared. The instrument was found to have been irreparably damaged by corrosion of the internal surfaces by the contents of the flue gas.

## CONCLUSIONS

- The results from the pilot scale investigations showed links between CO emission and degree of burnout and between CO emission and the levels of PAH detected. From this it is concluded that the link between burnout and PAH emission has been established for the rig used.
- The sampling regime for these tests was consistent for all the tests, it is therefore concluded that the PAH detected relate to the combustion conditions and are not controlled by the temperature profile for the gas path after entering the sampling probe.
- Higher levels of PAH are generated in combustion test facilities than in full scale boilers due to a combination of lower flame temperatures and shorter residence times. This makes monitoring of PAHs at full scale more complicated, and significantly increases the problems associated with sampling with the PAS2000 system, which was originally developed for an ambient monitoring application.
- The effect of the moisture content of the exhaust gasses, at the full scale tests, on the PAS2000 were damaging to the point of rendering the equipment useless.
- It is concluded that a more robust piece of equipment (not currently commercially available) would need to be designed to develop this methodology of assessing boiler efficiency on the basis of PAH measurements.

### Further information on the Cleaner Fossil Fuels Programme, and copies of publications, can be obtained from:

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## COST

The total cost of this project is £220,010, with the Department of Trade and Industry (DTI) contributing £110,005. The balance of funding was provided by the participants.

## DURATION

36 months - January 2002 to December 2004

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## FURTHER INFORMATION

For further information about this project see contractor report Real-Time Efficiency Measurements for Utility Boilers (REMUB) Report no. 295 URN 05/1683 available from the helpline.

