

**Fuel Sulphur Effects on Particulate
Emissions from Fuel Oil Combustion
Systems Under Accelerated
Laboratory Conditions**

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EXECUTIVE SUMMARY

The CANMET Energy Technology Centre (CETC)-Ottawa investigated the impact of fuel sulphur on emission characteristics for oil-fired combustion systems. Sulphur content is one of the key properties of fossil fuels that is related to their combustion characteristics including generation of pollutant emissions. The research program constitutes part of continuing cooperation between Natural Resources Canada and Environment Canada in reducing harmful emissions from stationary combustion equipment. The study results would provide additional scientific information for the Environment Minister's proposed agenda for cleaner engines, vehicles and fuels. Reducing sulphur content of petroleum based heating fuels has shown to reduce sulphur oxide emissions providing environmental benefits as well as longer service life of combustion equipment. Other benefits may also be gained from the use of lower sulphur fuels.

Due to an urgent need for research information within a limited time frame, CETC performed short-term exploratory investigations under accelerated laboratory conditions. The accelerated test program specifically examined emission performance of several distillate and residual heating fuels containing sulphur levels between 0.5 to 3.5% by mass. Test fuels were prepared by spiking different quantities of sulphur doping agent to a low sulphur diesel and two No. 6 fuels. A residential scale hot water boiler and a pilot scale rotary kiln furnace were employed as combustion equipment for the distillate and residual fuels respectively. Laboratory test parameters were strictly controlled to ensure the integrity and reproducibility of the results and a close simulation of field equipment conditions. Emission performance of the fuels, in terms of their particulate matter (PM) and gaseous emissions of O₂, CO₂, CO, SO₂ and NO_x, was determined and compared. The key fuel assessment tool used is the fine PM sampling system developed at CETC, capable of providing source PM concentrations that approximate ambient PM found in the atmospheric plume immediately downwind of the source. This unit offers particulate fractions containing PM_{2.5}, PM₁₀ and total PM, whose size and chemical properties were further examined. The PM_{2.5} and PM₁₀ are the size-segregated fractions representing PM smaller than 2.5 µm and 10 µm respectively. The presence of these fine

particulates in ambient air has been linked to adverse health effects. It is expected that this research would offer new information on how changes in fuel sulphur content affect the resulting PM characteristics that are eventually released to the atmosphere. In addition the results can be employed in mathematical modelling for source apportionment or determining the extent and type of the primary PM contributed by specific combustion sources.

Investigations on the heavy residual oils are continuing and therefore this initial report focuses on the results of distillate fuels only. A final report will be issued later to provide results from the heavy fuel combustion study. The results to date indicate that over the range of sulphur concentrations studied under selected experimental conditions, flue gas SO₂ emissions increased linearly with the increase of sulphur in diesel fuels, while other emissions including NO_x levels remained relatively unchanged. Similar elevation of filterable PM mass concentrations was also observed as the fuel sulphur increased. These results agree with the data reported in the literature for No. 2 and No. 6 fuel oils. The mass concentration results of PM_{2.5}, PM₁₀ and total PM fractions are very similar, within the experimental errors, suggesting that a majority of particulate emissions from diesel fuel combustion is in the 2.5 µm size range. The main constituents of filterable PM are soluble sulphates and carbon species, with only minimal amounts of inorganic elements detected. Soluble sulphates in PM increased with increasing fuel sulphur, while the PM total carbon species concentrations declined. Specific correlations between fuel sulphur and the sulphates and carbon contents of PM cannot be positively established at present, based on the limited data sets from this work. In addition, the effects of fuel sulphur on the distribution of organic carbon and elemental carbon species within the PM matrix were inconclusive. It is recommended that further investigations be carried out by including additional test fuels to obtain sufficient data for statistical analysis.

Size examination using transmission electron microscopy (TEM) revealed that the PM from all test fuels is mainly made up of very fine carbon particles approximately 0.05 µm in diameter. This agrees with the literature data, which report the size distribution of No. 2 fuel PM in the 0.02-3 µm range (1) and that of No. 6 fuel with a mean diameter of approximately 0.1 µm (2). However the type and operation mode of the combustor

significantly influence the PM characteristics as well. Due to the extremely small nature of particles, the computer controlled scanning electron microscopy (CCSEM) normally used for the PM size analysis was unable to provide useful information. TEM revealed the presence of two types of carbon structures, branched carbon chain agglomerates with individual rounded particles and clusters of rounded particles that are approximately 0.05 μm in diameter. The morphology of all PM fractions is very similar, suggesting that all particulates appear as $\text{PM}_{2.5}$. The TEM results cannot distinguish the effects of fuel sulphur on the particle characteristics.

Experimental data also provide reproducible PM mass balance data with minimum error margins. In the past CETC experienced technical difficulties in providing reliable data for low PM emitting fuels such as diesel and No. 2 type heating fuels. Through this work, PM source characteristic profiles for diesel and heating fuels normally used in residential heating become available. This new information is critically needed in source apportionment modelling of regional ambient PM since such data are currently unavailable. The PM assessment process being carried out for the Canada Wide Standards (CWS) would be able to use this information in identifying source PM contributions from the residential heating sector.

In summary, the study suggests that diesel based, light petroleum distillate fuels produce very small particulate matter approximately 0.05 μm in diameter during combustion in properly tuned residential heating appliances. Reduction of sulphur in heating fuels would reduce SO_2 emissions and filterable PM mass concentrations, provided that the combustion equipment is properly tuned and maintained relatively energy efficient. The sulphate content of particulate would decrease when fuel sulphur is reduced. While total particulate emissions may be greatly influenced by both the combustion conditions and fuel quality in non-optimized appliances, the high fuel sulphur content would definitely impact on the chemical composition of the PM, particularly sulphates and associated acids. The effects of fuel hydrocarbon types such as fuel aromatics on emissions were insignificant since the test diesel fuels contain similar hydrocarbon compounds.

CETC recommends that further studies be conducted to obtain comprehensive and relevant information pertaining to other variables, in addition to sulphur content, that

contribute to production of pollutant emissions. A better understanding of important variables that influence environmental and health impact would assist in developing clean and efficient combustion strategies.

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BACKGROUND

Under the federal government's integrated clean air strategy umbrella, Environment Canada fostered a multi-stakeholder consultation process in 2000 on "Future Canadian Emission Standards for Vehicles and Engines and Standards for Reformulation of Petroleum-Based Fuels" (3). Following a thorough review and full consideration of stakeholder comments, the department has developed a federal agenda of planned measures and future initiatives to reduce pollution from vehicles, engines and fuels. The minister's notice was announced in January 2001 (4). Measures to reduce the sulphur concentrations in light and heavy fuel oils used in stationary facilities are included as part of the key strategies in the department's comprehensive planned actions. Reduction of sulphur in on-road and off-road diesel fuels is also considered since the adverse effects of sulphur derived emissions from combustion sources on the environment has been widely documented (5). The proposed Sulphur in diesel fuel regulations will set a maximum sulphur limit of 15 parts per million in on-road diesel in June 2006. Regarding off-road diesel fuel, Environment Canada plans to recommend a regulatory sulphur limit that will be established in the same time frame than the U.S.. Throughout this important development process, the department continues to seek relevant information that would complement the quality and knowledge of science being applied in policy formulation of the regulatory actions. Natural Resources Canada participates in many levels of consultation processes under the integrated clean air strategy and cooperates with Environment Canada in areas of mutual interest.

At the international scene, efforts to strive for a cleaner environment is growing progressively, with increasing global awareness of the critical need to preserve sustainable environmental and economic development. Research and field data have shown significant benefits in emission reduction from combustion equipment by using higher quality hydrocarbon fuels or "cleaner fuels". In general, these fuels contain higher quantities of low molecular weight, aliphatic hydrocarbon compounds with minimum amounts of mineral matters than the average product. Fuels blended with large quantities of high molecular weight hydrocarbons such as aromatic compounds containing heteroatoms such as sulphur, nitrogen, phosphorus and other elements. These fuels tend

to have higher viscosity, density and final boiling temperatures than others and these properties have been linked to poor atomization problems during combustion. The large aromatic molecules are deficient in hydrogen and normally are difficult to combust leading to undesirable emission of incomplete combustion products. Numerous research data exist that demonstrated the benefits of using cleaner fuels for combustion, more information being available for transportation engine emissions. Regulatory authorities have promulgated increasingly cleaner fuel specifications and stricter emissions standards over the last few decades to reduce environmental pollutant emissions.

The CETC of Natural Resources Canada focuses on energy production and efficient and clean utilization of energy sources. Fuel assessment and emissions measurement research activities are among the key components of the many R&D initiatives of the Advanced Combustion Technologies Group at CETC. The research team has performed several investigations relating to fuel oil quality of middle distillate fuels associated with energy and emission performance of residential space and water heating appliances (6-19). CETC researchers and representatives from the Oil, Gas and Energy Branch of Environment Canada entered a joint research agreement of mutual interest that would provide critical scientific information in the implementation of the federal clean air strategy.

CETC proposed to examine the potential benefits of reducing sulphur content in heating fuels. The maximum sulphur limits of the test fuels were mutually set at 0.6% and 4.5%, respectively, for the distillate and residual oils. CETC also proposed that the assessment of the fuels would have to be carried out under accelerated and controlled laboratory conditions to meet the relatively short project deadline. Current petroleum distillate fuel for residential and commercial heating equipment has a maximum limit of 0.5% sulphur or 5000 ppm by mass as defined by the Canadian General Standards Board (CGSB) specifications. Low sulphur diesel for automotive and off-road applications has the maximum sulphur limit of 0.05% or 500 ppm sulphur. Emissions of sulphur dioxide (SO₂), sulphur trioxide (SO₃), nitrogen oxides (NO_x) and particulate emissions are of prime environmental and health concern and the fuels' performance can be measured in terms of these emissions. One of the potential emission benefits of using low sulphur fuels may be in the reduction of particulate matter (PM) including fine particulate

emissions. Fine PM is generally defined as the materials that are less than 2.5 μm aerodynamic diameter ($\text{PM}_{2.5}$) and those whose aerodynamic diameter is less than 10 μm (PM_{10}). Control or reduction of fine PM from various combustion processes is of particular interest to the departments since they have been linked to adverse health effects (20-23). CETC proposed to perform research using new methodologies to provide relevant information on the associations between fuel oil specifications and their emission characteristics. It is important to have new PM emission data for the CWS science assessment that is being conducted by Environment Canada. The existing emission databases that are developed using the traditional emission inventories are insufficient, in current form, in the identification of emissions from specific point sources. The research is intended to offer new information that is relevant to emission reduction strategies and sound science policy formulation.

This report describes the experimental procedures and methodologies used and the new information resulting from the joint study.

MATERIALS AND METHODS

EXPERIMENTAL FUELS

This investigation included five distillate heating oils or light fuel oils, containing sulphur mass from 0.05 to 0.6% and five residual fuels or heavy fuel oils with sulphur contents of 0.7 to 3.5%. **Table 1** shows an identification scheme for the experimental fuels for easy referencing. A commercial low sulphur diesel fuel was used as stock material to prepare the test fuels by adding a sulphur-doping agent, ditertiary dibutyl sulphide. The fuels contain nominal concentrations of 0.05, 0.1, 0.3 and 0.6% sulphur by mass. The fifth fuel is a regular No. 2 type heating fuel oil, normally used as a reference fuel in CETC investigations, whose combustion characteristics were established previously. The fuels are designated LD-500, LD-1000, LD-3000, LD-6000 and No. 2. Coincidentally, No. 2 fuel has 0.19% sulphur and therefore serves as the fuel with the median sulphur value, although it may contain higher amounts of relatively heavier hydrocarbons than the spiked diesel fuels. **Table 2** gives properties of the light distillate fuels.

For residual fuels, Environment Canada initially requested CETC to include commercial fuels containing natural sulphur as high as 4.5% by mass. However, CETC was unable to obtain fuels containing sulphur higher than 2.3 % although several fuel producers and suppliers across Canada and the Eastern US were contacted in search of such products. The Canadian producers contacted include Regina Co-op, Imperial oil, Petro-Canada, Shell Canada and Sunoco. Systematic sulphur spiking at CETC of two No. 6 type heavy fuels containing 0.7% and 2.3% mass sulphur produced two additional test fuels with 1.7 and 3.5% respectively. The reference fuel has a natural sulphur content of 1.97% by mass. Table 3 gives properties of the test fuels identified as HF-0.7, HF-1.7, HF-1.9, HF-2.3 and HF-3.5.

Table 4 gives concentrations of different hydrocarbons or hydrocarbon type information for all test fuels.

EXPERIMENTAL FACILITIES

Combustion Equipment

Figure 1 shows the combustion research facilities used for both light and heavy oil combustion work. These test rigs are designed and installed for assessing new combustion technologies, energy and emission performance characteristics of various fuels, combustion equipment and operating parameters. Typical features of a research rig include combustion equipment, heat distribution system, fuel delivery system, flue gas venting and control system, emission measurement equipment and data acquisition and analysis systems.

Light fuel oil combustion test facility

A cast iron boiler Model Starfire 3 manufactured by Utica Boilers of Utica, NY, USA was used. **Figure 2** shows a schematic of the entire test facility although only one boiler was used. The boiler is rated at 30 kW heat capacity and is equipped with a high efficiency, Beckett model AF 2 oil burner capable of operating with only a trace of smoke. The unit is located inside the constant temperature room that can provide similar temperatures for the test runs. Auxiliary components include a fuel feed system, the water circulation loop, make-up water and expansion tank.

CETC designed the water circulation system and pneumatic control valves to simulate realistic conditions of field water consumption by feeding the boiler outlet water through a heat exchanger, which artificially cools the hot water to normal return water temperatures. This entire water circulation system is computer-controlled using special data acquisition software with PID (proportional, integral and derivative) logistics. The boiler inlet and outlet water temperatures are set to be maintained at 54°C and 83°C respectively. These values reflect average temperatures for field units as reported in a study by Brookhaven National Laboratory of the US Department of Energy.

A flue gas venting system is used to exhaust the flue gases outside the laboratory through a steel flue stack connected at the boiler exit port. A barometric damper on the venting pipe controls the boiler draft and an induced draft fan on the pipe ensures positive removal of the gases. Sampling ports on the flue stack allow for measurement of boiler exhaust temperatures and emissions. These include ports for measuring the smoke

number, particulate sampling system probe, draft meter, flue gas temperature and sampling lines for gas phase emissions. The operation of the entire test facility is automatically controlled by a dedicated computer system in LabVIEW.

Heavy fuel oil combustion test facility

A pilot-scale natural gas fired, 90 kW rotary kiln furnace was used after retrofitting specifically for this work; **Figure 3** depicts a schematic of the boiler. The kiln is 4.27 m long with an I.D. of 0.41 m and an O.D. of 0.66 m. The material of the inside lining is a high temperature, erosion-resistant, castable refractory that can withstand temperatures of up to 1200°C. Draft in the kiln is controlled by a variable speed ID-fan. The standard emission control units for the kiln include an afterburner, multicyclone, bag house and a two-stage wet scrubber, although the bag house was not utilized during this work. The facility is monitored continuously for temperature, pressure and flue-gas composition by a dedicated computer and data analysis system using LabVIEW software. The kiln is ideally suited for process improvement studies such as waste combustion, incineration, minerals roasting, sintering, calcinating and thermal drying of solid fuels, slurries and concentrates. For this project an oil gun and a nozzle, equipped with a compressed air line to assist oil atomization, were installed while keeping the natural gas burner for preheating the kiln prior to oil firing. **Figure 4** shows a new heavy fuel delivery system, which was designed and installed on the kiln.

The heavy fuel oil delivery system comprises two 45-gallon drums, one positive displacement Mono pump, oil recirculation lines, a set of heated strainers with associated valves and flexible stainless steel lines and several thermocouples and pressure gauges to monitor the operation. Heavy oil is stored and preheated in one of the 45-gallon drums, while the other one is used to store No. 2 oil for cleaning the system after a test run.

Emission Measurement Equipment

Continuous emission analyzers: For both experimental test rigs, the following emission analyzers were used for gas phase emission analysis of O₂, CO₂, CO, NO_x and SO₂ concentrations in the flue gas.

Smoke number	True-Spot model RRB, Bacharach Instrument Co.
Particulate	Nutech Model 2010, EPA Method 5 stack sampling system
Oxygen	Horiba Model MPA 21A, paramagnetic analyzer
Carbon dioxide	Horiba Model PIR 2000, IR gas analyzer
Carbon monoxide	Horiba Model PIR 2000, IR gas analyzer
Nitrogen oxides	ThermoElectron Corporation Model IAR chemiluminescent analyzer
Sulphur dioxide	Western Research Model 721A

Fine particulate emission measurement system: CETC developed a prototype system for measuring fine particulate matter from pilot-scale boilers that burn fuel oil and pulverized coal (24-28). **Figure 5** shows the system that is specifically designed to collect fine particulates under simulated plume conditions that are comparable to the ambient particulates. The measurement system operation involves dilution of flue gas with purified air by 20 to 60 times inside a dilution chamber maintained at 40% relative humidity to allow for cooling and simulation of atmospheric transformation processes. Portions of the diluted gas are withdrawn, while maintaining isokinetic sampling of the flue gas, through selected cyclone and impactor inlets and filter packs to collect PM_{2.5}, PM₁₀, and total PM fractions. It should be noted that the PM_{2.5} fraction is collected using a cyclone, PM₁₀ by an impactor and total PM by collecting all particles directly on a filter inside a filter pack. Particulate samples are later analyzed in a receptor-comparable manner for mass, size distribution and elemental and organic carbon concentrations, soluble sulphates and acids using the appropriate analytical techniques. This sampling equipment is referred to as the source dilution system throughout the text.

EXPERIMENTAL PROCEDURES

Table 5 summarizes all laboratory procedures done during this research program. The exceptions are the literature review and the analytical procedures for determining fuel properties and for examining PM component characteristics such as size analysis, sulphates, carbons and trace elements. Please note that the preparation and optimization of test facilities and quality control procedures required more laboratory time than actual combustion and emission measurement experiments.

Literature Review

CETC's on-line search facilities were used to do a literature survey on the effects of fuel oil sulphur on energy and emission performance of combustion systems. Based on the information obtained, a summary report has been forwarded to Environment Canada under separate cover.

Fuel Analysis Procedures

Tables 2 to 4 give an analysis of all test fuels following standard reference procedures. Of these parameters, sulphur content, viscosity and density are among those specified in the Canadian General Standards Board (CGSB). Although not designated in the CGSB specifications, hydrocarbon type constituents were investigated to gain more fuel property information. For distillate fuels, supercritical fluid chromatography (SFC) was used. The heavier No. 6 fuels require a different test method called SARA procedures to determine saturates, aromatics, resins or polar compounds and asphaltenes. SFC is not suitable for fuels that have final boiling points higher than 450°C. The elemental composition of heavy fuel oils was also determined using inductively coupled plasma emission spectroscopy. After preparation of spiked fuel blends to obtain the required sulphur levels, each was analyzed to determine the actual concentrations.

Laboratory Facility Preparation

Careful execution of this task was essential in ensuring proper working order of the facilities, especially the combustion units. The units must be able to provide reliable

and consistent performance during fuel comparison tests. Preparation of supplies, materials and equipment for the test rigs, fuel blends, sampling systems and data acquisition units required a considerable amount of effort, planning and coordination.

Residential scale oil-fired boiler

The standard 6-in. diameter flue pipe was initially replaced with a specially designed 3-in. tapered pipe to increase flue gas velocity. Combustion units with flue gas velocities lower than 3 m/s usually present problems in isokinetic sampling of particulates and it is desirable to attain a high velocity. However, initial tests using the smaller flue pipe revealed that it was extremely difficult to maintain and automatically control the boiler stack draft, although velocities higher than 3 m/s were obtained. It would also require additional time and resources to improve the draft control system for the retrofitted unit until reliable conditions can be maintained. Since maintaining a consistent performance of the boiler is very important throughout the test program to allow for fair evaluation of different test fuels, the trial test plan was terminated. The standard flue pipe was reinstalled and reoptimized for the experiments.

Rotary kiln furnace

Preparation of this unit presented greater challenges than the residential unit since it involved modifying a natural gas fired system to a dual-fuel firing unit for heavy oil application. The efforts were somewhat hampered by necessary repairs on the oil delivery pump. Several trial experiments were necessary in optimizing the heavy oil delivery system. Operational difficulties were experienced in selecting a proper oil nozzle size, in controlling and maintaining a constant oil pressure to the oil gun and in optimizing the combustion air supply.

Fine particulate emission measurement system

The fine PM sampling system was thoroughly cleaned, inspected and its flow measuring equipment was calibrated. A number of trial experiments were later conducted to optimize sampling conditions to satisfy the PM sample requirements for all laboratories for their respective analytical protocols. For example, the SEM laboratory

requires a single layer PM deposition on the filter while the carbon analysis filters need to be at the specific shade of darkness. It is critical that PM filter samples be supplied to the laboratories to satisfy the specified conditions for each analysis. This will ensure that the results are meaningful and reliable.

Necessary actions were taken to ensure that the sample-to-air dilution ratio was accurately measured and properly controlled during fine PM sampling. CETC used a CO₂ tracer method to accomplish this goal. This involves accurate measurement of concentrations of CO₂ in the flue gas, dilution air and the mixed sample inside the dilution tunnel. A 3-channel CO₂ analyzer was specifically installed for this purpose. The unit was operated manually at first but the associated operating software was later modified to allow automatic control of flow measurements. Accurate control of the flue gas and the dilution airflows is necessary to keep the flows balanced, while maintaining isokinetic sampling.

Combustion and PM Sampling Experiments

Light distillate fuel combustion procedures

The test boiler was commissioned using a reference No. 2 heating oil and its performance characteristics were examined. Burner setting was optimized by adjusting the combustion air to obtain a smoke trace on a test paper between No. 1 and No. 2, according to the Baccharach scale. The Baccharach smoke number is normally used by the oil heating industry as a qualitative indicator of relative PM emissions from a given burner/appliance combination. It should be noted that one specific number may not represent the same combustion condition when comparing across burner/furnace combinations. Although the burner used in the test boiler is capable of operating at a trace smoke level, this setting was chosen to reflect field use and also to shorten the PM sampling time. Most surveys of field burner settings indicate a wide variance in smoke numbers and most of them show smoke levels higher than number 2. More important, this selected setting provided very low excess air and high efficiency conditions at CO₂ concentrations of 12.5-12.9% and O₂ concentrations of 3.5-4%. This setting provides a dynamic appliance efficiency of about 83%, which is approaching the optimum conditions for a residential oil-fired boiler. Therefore, all fuels are evaluated after the

burner is adjusted each time to attain the best CO₂ and O₂ levels selected above. This criterion is considered the best compromise for this experimental work. Adjusting the burner at the same combustion air supply will not necessarily provide the best and fair operating conditions for all fuels since each fuel has optimized conditions that are different from the others. In other words, a cleaner burning fuel may be unnecessarily compromised in its air setting if it were operated under the same conditions selected for an average or poor-performing fuel.

The boiler operating procedures for a test fuel was selected to include a short cycle emission monitoring run and one continuous boiler “on” period, during which PM measurement was performed using the source dilution sampler. The short cycle test has a 1 h steady state burner “on” mode followed by five 10 min “on” /10 min “off” cyclic operation. This procedure has been used as a reference test pattern at CETC and is believed to best represent the average home appliance operation in central Canada. The fine PM measurement procedure usually requires 20-45 h of continuous burner “on” operation, depending on the PM emission generated by the fuel. At least three experiments for each fuel were conducted under both the short cyclic operation and the long PM sampling procedures. Both procedures required an initial 1 h steady state boiler operation to allow for stabilization of experimental conditions. As a prerequisite, trial combustion experiments are usually carried out for each fuel to determine the approximate sampling period for the collection of sufficient PM for subsequent analyses.

A typical combustion experiment follows the protocol outlined below.

- Fill fuel drum with the selected test fuel and flush the system to avoid cross-contamination and maintain temperature in the test room between 17°C-20°C.
- Initiate “analyzer calibration program” and calibrate analyzers for monitoring of CO₂, SO₂, NO_x, O₂ and CO stack emissions.
- Calibrate stack draft and over flame draft manometers and pressure transducers.
- Start “data acquisition and control program” for burner operation and emissions monitoring. Select the operation mode for steady state and cyclic conditions (for short-term emission monitoring) or extended burner “on” operation for fine continuous PM sampling.

- Turn on damper, cooling water and control valves for boiler operation.
- Start burner and allow for stable conditions for about 45 min.
- Adjust burner setting to achieve required emissions and smoke number.
- Perform the short cyclic combustion experiment.

Source dilution sampling system preparation

- Condition filters for 24 h in advance inside the humidification chamber maintained at 40% relative humidity (RH).
- Weigh filters and load in filter packs on the dilution sampling system.
- Determine boiler stack conditions and flue gas velocity.
- Determine the required dilution ratio and residence time.
- Calculate total volumetric flow (dilution air and stack sample),
- Select nozzle size to accomplish isokinetic sampling.

Test Procedures

- Run calibration program to calibrate two CO₂ analyzers dedicated to measuring the CO₂ in the dilution air and the mixed sample inside the dilution tunnel.
- Insert probe into stack at the proper position and turn on probe and mixing chamber heater.
- Run “data acquisition and control program”.
- Run dilution sampling for required sampling period.
- Remove filters and condition them inside the humidification chamber for 24 h.
- Weigh filters and calculate sample weight (mg) and loading (mg/m³ flue gas).
- Repeat test procedure after placing appropriate filters for the other selected PM analysis procedures. Note that analysis techniques require the use of specific filter media and sample loading on filter.
- Label and send filters to analytical laboratories for various analyses.

Heavy residual fuel combustion procedures

The procedures commence with pre-firing the kiln with natural gas at least 5 hours prior to the No. 6 oil firing. This allows for the gradual increase of refractory

temperatures before it reaches the operating conditions. The fuel oil has to be heated to the operating temperature several hours in advance as well before operating the fuel firing system. After priming, the fuel pump (Mono pump) is turned on and circulation of heavy oil is established. Oil recirculation between the pump and the holding drum mixes the fuel and maintains the temperature at approximately 60°C. The fuel delivery line from the pump to the oil gun is also preheated and its temperature is controlled at approximately 48°C. Once the refractory temperature in the kiln reaches 550°C, the oil gun is inserted through the opening near the gas burner. The natural gas firing is stopped and heavy oil is fired. The air atomizing pressure is adjusted and controlled with a pressure regulator at approximately 186 kPa (27 psig), to provide good atomization and match the corresponding fuel delivery pressure to the gun. Oil temperature and pressure at the tip of the gun is critical for efficient atomization and good combustion. Burner oil pressure is controlled between 55-103 kPa (8 to 15 psig) by the bypass recirculation return valve and a second needle valve. Adjustment of the oil pressure is necessary during the test run to accommodate the gradual increase of fuel pressure at the tip of the gun due to char deposition.

Emissions Measurement

Emission measurement from the kiln and the residential boiler applied similar laboratory procedures and therefore the following protocols describe the operations for both systems.

Gaseous emissions

Gas phase emission concentrations of O₂, CO₂, CO, NO_x and SO₂ in the boiler and kiln flue gas were continuously monitored using the continuous emission analyzers described above. The data acquisition software provides emission and temperature profiles for both steady state and cyclic operations that are characteristic of energy and emission performance of a combustion process. Results from triplicate runs are averaged to represent emission data for a test fuel and are used for comparison with those of the others.

Particulate emissions

The widely used traditional means of measuring total particulate mass emissions from stationary combustion systems is the EPA Method 5, commonly known as the M5 method. The reference protocol employs the collection of particulates under high temperature conditions, normally at 121°C, to avoid sample condensation but does not allow for simulation of atmospheric transformations as in the case of source dilution sampling. However, it has been an industry standard for decades and the resulting information can easily be compared with the existing emission inventories, while source dilution sampling results are still relatively scarce. The M5 procedures for direct source PM emissions were applied for two fuels only, the 560 ppm diesel and the reference No. 6 fuel oil. It should be noted that although both methods employ isokinetic withdrawal of flue gas samples, the M5 procedure involves collection of all particulates on a single filter, while the source dilution procedure collects much smaller portions of diluted flue gas through multiple filters. Therefore only a general comparison can be made if the results are expressed in terms of PM mass concentrations in a unit volume of flue gas sample collected.

Characterization of particulate emission samples

Figure 6 outlines procedures used for comprehensive analysis of filterable particulate sample for all emission measurements performed. The protocol is developed with special emphasis on the ambient or receptor-comparability of the PM characteristics to ensure that the source data can be used in source apportionment of the ambient PM concentrations.

Particle size distribution was examined by CCSEM and TEM; trace elements were determined by energy dispersive X-ray fluorescence (XRF); organic and elemental carbon contents by thermal-optical reflectance procedure and particle bound acidic species such as sulphites, sulphates, nitrates and hydrogen ions by ion chromatography (IC). Mass determination of all PM fractions was carried out by gravimetry using a microbalance inside a humidity-controlled chamber maintained at 40% relative humidity.

RESULTS AND DISCUSSIONS

COMBUSTION RESULTS FOR DISTILLATE FUELS

Optimization of Combustion Parameters

Boiler operating conditions were established to ensure that the experimental fuels were assessed without bias and that the results provided meaningful conclusions. Combustion experiments were therefore conducted under similar operating conditions for all fuels. Table 6 gives the results. The emissions and temperatures in the table represent the average values of the monitored data from the extended boiler “on” run during which PM sampling took place. The data show similar CO₂ and O₂ concentrations for all test fuels, which indicates that comparable boiler operating conditions were established. Similarly, comparable dynamic efficiency and excess air data were obtained for all combustion experiments. All fuels showed approximately 87% efficiency under controlled test conditions. This demonstrates that these fuels would perform well in the field providing energy savings to the homeowner if the appliance is tuned properly.

Emission Performance of Fuels

Light distillate fuels

Figure 7 (a) to (g) shows a series of temperature and emission profiles for a typical combustion run of LD-500 fuel. These graphs illustrate the stability of the steady-state boiler operation and the reproducibility of cyclic emissions. **Appendix A** gives similar profiles for the remaining fuels. **Table 7** summarizes averaged volumetric emission concentrations for all test fuels for 1 h steady state and five cyclic operations. The data indicate good reproducibility for the same-run and between-runs. The results suggest that gaseous emissions from the test fuels are similar except for the SO₂ concentrations that increased with the increase in fuel sulphur.

To evaluate emissions under comparable conditions, the results were normalized at 3% oxygen and are presented again in **Table 8**. NO_x emissions do not appear to be influenced by the variation of fuel sulphur within the selected study range. In fossil fuel combustion fuel nitrogen content and combustion zone temperatures are main factors in

the production of NO_x. The fuel nitrogen content of the test fuels does not vary significantly and therefore its effects can be considered minimal.

The combustion zone temperature during the experiments was not expected to vary since the burner operating conditions for all test fuels were found to be relatively constant, including the excess air setting. However, the properties of the test fuels are very similar and any drastic change in the excess air requirement is not expected. In summary, the test fuels are not sufficiently different from each other to warrant a noticeable variation in NO_x emissions.

Figure 8 shows the effect of fuel sulphur on SO₂ emission. A linear positive effect of the fuel sulphur is noted. This phenomenon was observed during previous CETC studies that examined the 0.01 to 1.2% fuel sulphur range.

Particulate Emissions

CETC has in the past experienced difficulties in attaining reproducible results from the combustion of low emitting fuels such as low sulphur diesels and No. 2 oil, although reproducible results were obtained for high PM emitters such as residual oils and pulverized coal. The protocol was improved by applying longer sampling times that extended overnight to obtain sufficient samples for gravimetric analysis. For example, a 45 h sampling was applied for the LD-500 to provide reproducible gravimetric analysis results. Another significant improvement in the sampling procedure was realized when the CO₂ tracer technique was introduced to allow for accurate measurement and control of the sample dilution ratio. Maintaining a consistent dilution ratio during source dilution sampling ensured good reproducibility of the PM mass data.

Figure 8(a) to (g) shows typical emission and temperature profiles recorded during a source dilution sampling experiment for LD-1000. It also demonstrates the capability of the data monitoring and analysis sub-routine of the CETC developed computer software. The program provides similar graphics of all operation time-based profiles of temperature, emissions and process variables. Reproducibility of these profiles for multiple runs is usually within 5-7% margin of error.

Table 9 gives PM emission results. Results are expressed in terms of filterable PM mass in mg/m³ dry flue gas at standard temperature and pressure. Each sampling run

collects two filter samples for PM_{2.5} and PM₁₀ fractions and one for the total PM fraction. Data for all replicated runs are given along with the calculated relative standard deviation. PM mass concentration results are reproducible within the same run as well as for replicate runs, although the absolute mass of particulate samples usually weighs about 250 to 1000 µg per filter.

A research project performed at the US Environmental Protection Agency (USEPA) laboratories reported a total PM concentration of 6.1 mg/m³ for a fire tube boiler fired with No. 2 fuel containing 4000 ppm sulphur (29). CETC results are in line with this literature value although the 70 kW EPA boiler is slightly bigger than the CETC unit, which is rated at 30 kW. The average mass loading for LD-500 is about 2.01 mg/m³ whereas the results by the M5 method showed 1.77 mg/m³. Since this is the only dataset, no definite conclusions can be made.

Table 9 notes the apparent similarity of the mass concentrations for all PM fractions for a fuel. This suggests that all particulates emitted from distillate fuel fired residential boilers fall in the PM_{2.5} fraction. This is only true for fuels containing up to 6000 ppm sulphur based on the observations from this study. Similar studies done for transportation and mining engines reported that diesel fuels normally generate very small particles less than 1 µm in diameter, known as ultra-fine PM. Previous research at CETC using No. 4 type residual fuel oil showed the presence of about 10-15% of particles larger than 10 µm, in addition to PM_{2.5} and PM₁₀. This will be discussed later when the PM size characteristic data are presented.

Data in **Table 9** also reveals that the filterable PM mass concentrations increased with increased fuel sulphur content. This is demonstrated in **Figure 10** for the total PM fractions. **Figure 11** shows another that represents the PM_{2.5} and PM₁₀ fractions. The similarity of the results for all PM fractions makes it difficult to present all data points in one graph. The results for No. 2 fuel oil also fall within the data set although its fuel matrix is slightly different from those of diesel fuels. This observation appears to suggest that reduction of fuel sulphur could reduce particulate emissions from oil-fired residential heating units provided the equipment is properly maintained and operated. Units that are functioning improperly would generate high levels of pollutant emissions and the effect of fuel quality on emission performance may not be apparent.

PM size and morphological characteristics

Initial size analysis of PM samples revealed the apparent difficulty in size measurement since the particles are extremely small and largely agglomerated, forming long carbon chains or clusters. The laboratory reported that TEM had to be applied for these samples since the CCSEM technique would not provide accurate size data. TEM involves penetrating a high-energy electron beam through the sample, while the electron beam only scans the sample surface in CCSEM. TEM also applies much higher magnification of the images and thus provides more detailed information than the CCSEM. However, since it is a manual method, unlike the CCSEM, measuring the mass distribution of individual particles is extremely difficult. **Figure 12** shows a sample electron micrograph at an 85,000 magnification of a PM_{2.5} sample from LD-500 fuel. **Figure 13** shows an overall field image of the same sample at 5,000 magnification. The clear droplet-like images are the pores of the filter media and only the opaque or dark images represent particulate materials. The darker the image, the thicker the PM. The laboratory confirmed that these dark particles are mainly carbon and that two morphology types were observed on all samples analyzed. The first type was the branched carbon chain agglomerate with round particles predominantly in 0.05 µm in diameter. The second type represents clusters of round particles of comparable size. In addition, no distinction could be made between the PM_{2.5}, PM₁₀ and total PM samples or between those collected from the combustion of different test fuels. **Figure 14** shows the elemental spectrum of the sample. Only the background signals show no measurable quantities of elements were detected. The two large clusters of peaks in the spectrum represent copper from the metal screen on which the sample image is prepared for the analysis. Detection of sulphur on a PM filter sample by TEM is inherently difficult since the high-energy electron beam tends to accelerate the sublimation of sulphur. The laboratory could not distinguish between the PM samples collected from the fuels containing different amounts of sulphur. These observations suggest that all distillate fuels used in this study produced mainly carbon particles in the 0.05 µm size range. **Appendix B** presents additional TEM images of PM samples for other test fuels. Previous research at CETC showed that No. 4 type residual fuel oils generated particles that are mainly carbon rich in nature and sulphur is the second most abundant element

(27). About 75-90% of the PM is PM₁₀ and about 50-75% is PM_{2.5}. In addition the filter samples contain about 10-15% of particles that are larger than 10 µm.

PM chemical composition

A better understanding of the chemical constituents of ambient particles is fundamental in bridging the knowledge gap between the air quality and its health effects. The acids and toxic trace elements found in fine PM have been linked to a few known illnesses in humans and research animals. It has been suggested that the extremely small size of the fine PM promotes efficient entry and adherence to the lungs and the toxicity of the particles are mainly responsible for inflicting damage to the organ. Ambient fine particles are generally made up of numerous species depending on the sampling location. These include acidic species such as sulphates and nitrates that exist as ammonium salts, carbon species, water, trace elements mainly in the form of oxides, earth crustal matter and other airborne fragments of natural and anthropogenic origins. Combustion of fossil fuels is known to generate source PM mainly composed of carbon species, condensed acidic species and trace elements. The CETC protocol examined these source PM constituents and the results are presented.

Combustion generated particulates contain several oxides of mineral matter as contributed by the elements contained in the original fuel matrix. **Table 10** reports the concentrations of trace elements found in particulates as determined using the XRF technique. **Table 10** represents only the five most abundant elements although a total of 25-35 elements were determined. The remaining elements were below the instrument's detection limit and therefore omitted. Data clearly indicate the absence of any measurable elements in the filterable PM. The very low, but similar concentrations of Si, P, S, Fe and Sn are noted in all samples regardless of the PM fraction or the sulphur content of the fuel. In other words, only minute quantities of trace elements are generated during combustion of diesel and No. 2 fuel on residential heating equipment. This can be expected since most of the light and middle distillate fuels contain only minute amounts of inorganic trace elements. This is different from the previous data obtained from the combustion of No. 4 fuel oil where moderate quantities of V, Ni, S, Ca, Si and Fe were found to exist as trace elements.

Sulphates and nitrates in PM are formed during the secondary PM formation process when primary PM such as SO_x and NO_x undergo gas-to-particle transformation process. Sulphuric and hydrochloric acids also condense on PM surfaces but usually are detected as soluble sulphate and nitrate ions when the samples are dissolved in water. No appreciable nitrates were detected in the samples from this study due to low concentrations of nitrogen oxides present in the flue gas. As described in **Figure 6**, soluble sulphate and hydrogen concentrations of the PM samples were determined by aqueous extraction of the filter materials.

Table 11 reports the pH and sulphate concentrations of the PM samples analyzed. The pH values represent hydrogen ion concentrations contributed by condensed sulphuric, hydrochloric and nitric acids that are derived from gas phase SO_2 , HCl and NO_x species. **Figure 15** shows an apparent positive effect of fuel sulphur on the PM sulphate with the exception of LD-6000. Similar observations have been reported on the effects of fuel sulphur on SO_2 and sulphate formation in oil-fired boiler emissions (16, 17). As for the unusual behaviour of the LD-6000 fuel, additional experiments conducted to verify the results have confirmed the findings. This appears to suggest that the SO_2 to sulphate conversion and condensation on filters become relatively constant at the 3000 ppm at the operating conditions described above. This assumption could be confirmed by conducting additional experiments using diesel fuels containing sulphur concentrations greater than 6000 ppm. However, the important message is that combustion of higher sulphur fuels would produce a higher PM sulphate content. The release of these particles into the atmosphere will inadvertently contribute to highly acidic ambient PM concentrations.

Combustion derived particulates contain organic carbons (OC) and elemental or graphitic carbons (EC), the latter being a key contributor to the atmospheric visibility degradation. Organic carbons are associated with numerous and complex organic species, some of which are known air toxic compounds. Organic carbons are generally contributed by unburnt fuel hydrocarbons and elemental carbons are usually the product of fuel pyrolysis during combustion. It has been reported that industrial oil-fired combustion systems tend to generate more elemental carbons than organic species,

although their actual concentrations in PM highly depend on many variables including the combustion process itself, unit configuration, operation mode and fuel composition.

A commonly used technique for OC/EC analysis involves optically monitored combustion of carbons at different temperatures followed by conversion to methane and quantification using a flame ionization detector. The analysis, however, is method defined and is associated with inherent inadequacies that could lead to unsatisfactory results under poorly controlled sampling conditions. Therefore, CETC performed trial runs to determine optimum conditions for both OC and EC analyses. This was done for each test fuel, in consultation with the analytical laboratory. However, the analytical method is extremely sensitive to the level of sample darkness on filter and there could have been some uncertainties in the OC and EC results.

Table 12 summarizes CETC research data, where OC, EC and total carbon (TC) content of the PM samples are reported. Although it appears that fuel sulphur has no or little effect on organic and elemental carbon species in PM, OC is slightly higher than EC in most cases with the exception of LSD-500. The high OC/EC values can be interpreted as an indication of clean and efficient combustion. Light distillate fuels such as these burn cleanly without leaving unburned carbon deposits such as elemental carbons. However, CETC believes that there may be large uncertainties associated with this fuel since it was the first sampling trial for the operator. For example, inconsistent analytical results were received for four filter samples with different PM loading from the same experiment using LD-500 fuel. From the data, total carbon concentrations in PM appeared to decrease when fuel sulphur increased. This general reduction of carbon percentage in PM is to be expected since the percentage of sulphate in PM progressively increases as the fuel sulphur increases.

PM mass balance

The following general assumptions are made in calculating the composite mass balance data or speciated PM data. In any particulate sample metals exist in the form of oxides, most of the sulphur is in the form of sulphate, organic carbon species contain some non-carbon atoms, and water of hydration exists. In this work, water of hydration is

added to the sulphate concentration using the reference formula reported by the Society of Automotive Engineers (30).

In coal and heavy fuel combustion systems, water of hydration in PM is usually associated with mineral matter. In the case of PM whose elemental content is extremely low such as in the diesel particulate, water of hydration is mainly associated with sulphate molecules. CETC confirmed this assumption with the Emissions Research and Measurement Division of Environment Canada.

Organic carbons represent several complex organic compounds containing heteroatoms such as oxygen, sulphur and nitrogen and the total corresponding mass is assumed as 1.6 times that of the measured OC. Elemental carbons require no correction in mass calculation since most of them exist as pure carbons. However, the corresponding mass for metal oxides is calculated as twice that of the total elemental mass, assuming that metal oxides exist as M_2O , MO , M_2O_3 and M_2O_4 . By applying these assumptions, calculation of the data in Tables 11, 12 and 13 provided composite particulate mass balance results in **Table 14**. The averaged results from multiple runs were used in these calculations. Results indicate a relatively comparable agreement between the composite mass or speciated mass data and the actual mass data from gravimetric analysis. In addition, a very good reproducibility between the experiments for each fuel as well as for each PM fraction was noted. Due to inherent problems associated with very small quantities of PM mass, it is very difficult to obtain reproducible results with a good mass balance for low PM emitters such as low sulphur diesel fuels. In the past CETC has obtained mass balance results for high PM-emitting No. 4 fuels with higher degrees of agreement between the composite values and the determined values (27).

PM source profiles

Table 15 presents a typical PM source profile data for LD-1000 fuel. CETC believes that this new information reveals, for the first time, size-resolved PM compositions that would be found in the atmospheric plumes at residential areas during the heating season. These plume-like concentrations, not the stack emissions, truly represent types and quantities of air emissions to the regional air shed from local point sources. These profiles represent signature characteristics of air emissions that are specific to source

type, depending on the fuel, combustion system configuration and mode of operation. They are also known as source signatures. Contribution share from each source to the regional air quality can then be determined using mathematical source apportionment modelling techniques, which also incorporate regional ambient PM emission profiles measured at the receptor site.

Applicability of the data to source apportionment modelling

To emphasize the usefulness of source profiles in receptor modelling of ambient PM at the Canadian air monitoring sites, understanding of the complex associations of atmospheric and source particles is essential. The following discussion is included to provide such knowledge, although brief, and to fully appreciate the potential application of the data to Environment Canada's CWS (Canada Wide Standards) development process.

Current air pollution monitoring data show that ambient PM_{2.5} portion contains a large fraction of secondary particulate matter that was formed in the atmosphere and is composed primarily of sulphates, nitrates, condensed organics, carbonaceous matter and inorganic aerosols of trace elements found in fuels. These secondary particles are formed by chemical transformations of primary emissions such as SO₂ and NO_x and other secondary PM precursors such as NH₃ and ozone. PM₁₀ tends to be dominated by particulate materials that were directly emitted into the atmosphere, which are also known as primary particulates. Because PM_{2.5} is generally considered more critical in PM related health impacts than PM₁₀ and the secondary particle formation in PM_{2.5} is extremely complex, it has become apparent that models that are developed for determining source-receptor relationships must take this secondary PM into account. It is important to know whether composition and size characteristics of PM from different sources are sufficiently distinct that one can detect their components by analyses of ambient PM and if so, one needs to know which species yields the clearest distinctions. In general, these questions are answered by numerical modelling by least-squares fit using the source profiles from the sources and the ambient PM. However, since the early 80s, it has been established that many existing stack-particle data are representative of

neither the size distribution nor the chemical composition of stack particles after they reach the atmosphere (31-33).

Based on initial source identification studies carried out by the US EPA, stack PM emissions data that are traditionally obtained from baghouse dust, in-stack samplers or M5 equipment were reported as not detailed enough for chemical mass balance modelling for source apportionment. These methods, unlike the source dilution approach, usually exclude condensation, vaporization, agglomeration and secondary chemical reactions of stack aerosols. Subsequently, the source dilution sampling approach has become the accepted method for developing source profiles or source characteristics of size-resolved PM emissions from specific point sources.

In addition, modelling is assisted by selection of marker elements and species. For example, V and Ni are obvious markers for oil combustion source, Zn for refuse combustion, Na for sea salt or marine sources, Ca and Mg for limestone and Al, Fe, Ti, Se for coal combustion and soil crustal matter. Environment Canada's Emission Research and Measurement Division is currently conducting research on application of organic chemical markers for auto vehicle emissions. CETC has developed initial source profiles for No. 4 fuel and pulverized coal combustion using pilot-scale boilers.

We believe the results from this study supplement the existing database. They also demonstrate the great potential of the new PM measurement methodology in establishing source profiles for the residential heating sector that will be an integral part of source-receptor relationships. This will certainly provide new scientific information to Environment Canada's PM assessment process.

COMBUSTION RESULTS FOR RESIDUAL FUELS

Text will be completed later after completing the combustion experiments using No. 6 test fuels.

SUMMARY AND CONCLUSIONS

The following conclusions can be made from the accelerated short-term laboratory study.

- The residential scale oil-fired boiler test facilities at CETC provided reliable combustion performance and reproducible emission data for this research project. However, a significant amount of time and effort was required in preparing the test facilities and incorporating control systems to ensure that test fuels can be assessed under similar and consistent experimental conditions.
- The natural gas fired rotary kiln furnace selected for combustion of heavy fuels required modifications to the burner and fuel system in retrofitting the unit into a dual fuel system. However, the high temperature combustion zone and long residence time inside the kiln appeared to promote efficient carbon burnout, resulting in generation of mineral laden PM. The inherent high excess air conditions of the system also created very lean combustion environment, emitting relatively low PM concentrations. To ensure that the experimental conditions closely resemble field operating scenarios, CETC explored the possibilities of using another heavy fuel firing furnace, which recently became available. Experiments will resume using the combustion system that closely met the criteria and a report will be prepared after the tests are completed.
- Under the experimental conditions reported above, combustion characteristics of the five light distillate oils containing 0.05% to 0.6% sulphur by mass were similar, with the exception of SO₂ emissions. Flue gas SO₂ emissions linearly increased with fuel sulphur content. Similar observations were noted for No. 2 and No. 4 fuel oils during previous studies at CETC and the US Department of Energy.

- Flue gas nitrogen oxides or NO_x and CO emissions did not change significantly when the fuel sulphur was increased. The fuel nitrogen content of test fuels and combustion conditions did not vary sufficiently to warrant any noticeable change in emissions.
- All test fuels, being light petroleum distillate oils, burned cleanly and produced very low PM emissions. As a result 20-45 h sampling periods were necessary to collect sufficient PM samples for subsequent analyses. Recent modifications made to the CETC fine PM measurement system has provided reproducible PM results which were difficult to achieve in the past.
- All distillate test fuels produced emissions mostly in the fine PM_{2.5} range. The concentrations of PM_{2.5}, PM₁₀ and total PM were essentially the same.
- TEM analysis of the PM samples revealed that distillate fuel generated PM are mostly carbons that are very small, approximately 0.05 µm in diameter. Two types of carbon structures exist, chain like agglomerates and carbon clusters. The morphology of all PM fractions is similar. The PM from different test fuels also shows similar characteristics and the method could make no distinctions between the particles with respect to the fuel sulphur content.
- Under the selected experimental conditions, test fuels containing successively higher sulphur produced proportionately higher filterable PM emissions. This suggests that reducing fuel sulphur content in heating fuels would reduce PM emissions from residential appliance, providing long-term benefits on the environment, energy efficiency and appliance integrity.
- Analyses of PM showed that organic and elemental carbon contents are similar for most fuels. The analytical method is extremely sensitive to the extent of sample darkness on filter and there could have been some uncertainties in the OC and EC results. However, total carbon concentration results appear to indicate a gradual decline in carbon content in PM when the fuel sulphur was increased.
- The sulphate content of the filterable PM generally increased with the elevation of fuel sulphur content but appeared to have plateaued at the 3000 ppm level. A similar levelling effect in total carbon content of the PM at the 3000 ppm level was observed. Additional experiments using LD-6000 fuel provided similar observations, thus confirmed the original data for the 6000 ppm fuel. However, it would require

additional data sets at different sulphur concentrations, for example, those higher than 6000 ppm, and some between 500 and 3000 ppm to make logical data interpretation and specific conclusions. CETC therefore recommends that additional investigations be carried out to satisfy this need. At present, we can state with certainty that increasing the sulphur content of distillate fuels would produce particulates with higher sulphate concentrations during combustion.

- Very minute quantities of trace elements were detected in the distillate fuel generated PM since these fuels do not contain substantial amounts of mineral matter.
- Generally, distillate fuels combusted in properly maintained residential heating equipment produced particles in the sub-micron range that are mainly made up of carbon, sulphates and associated water. This was confirmed by the PM mass balance results.
- CETC provided new PM source characteristic profiles for low sulphur diesels specific to residential heating that can be incorporated in the regional air quality modelling.
- In summary, using low sulphur heating fuels would provide measurable benefits in reducing SO₂ air emissions and its oxidation product, sulphate. Reducing the release of these species into the atmosphere could reduce acid deposition and the acidity of the ambient fine PM. Sulphate is a major component of airborne PM and its exposure to human population in high concentrations has been associated with lung cancer and other pulmonary illness such as bronchitis and asthma. Therefore the use of low sulphur fuels in residential space and water heating could benefit the environment as well as human health. Another advantage is reduced acid condensation on combustion equipment components and venting systems thereby reducing corrosion damage.
- It is recommended that additional studies be designed and conducted to further these important investigations. Time allotted for this study was rather limited and subsequently affected the outcome of the work. The study should include fuels with a wider range of sulphur and, more important, select fuels with realistic hydrocarbon matrix that would represent actual heating fuels, not diesel fuels. This may require preparation of specific fuel blends at a refinery since commercial heating oils would not cover a wide range of fuel sulphur.

EXPERIMENTAL PROBLEMS AND DELAYS

The CETC team experienced several technical problems and delays during the course of this project. Following is a description of some of the events worth reporting.

- The project leader felt that the time allotted for this research project was insufficient. However, considerable effort was made to complete the project on time. If more time were available, the research team would have performed additional experiments to gain valuable information. It is hoped that CETC will have future opportunities to conduct such worthwhile investigations.
- The installation of the heavy fuel delivery system for the rotary kiln was seriously delayed due to necessary repairs on the fuel pump. The servicing company could not find the necessary parts locally and it took much longer to order the parts from the manufacturer. This seriously delayed the fuel system installation and evaluation of the retrofit burner performance. The subsequent boiler commissioning and optimization procedures were also affected, causing delays.
- About six weeks was necessary for calibration of the mass flow controllers on the fine PM measurement system since the procedure had to be performed at a specialized company. Accurate performance of flow control equipment is critical in quality assurance of the laboratory procedures, CETC pursued the calibration despite the unnecessary delays.
- The local supplier miscalculated the low sulphur diesel order and delivered lower than expected quantities. This restricted CETC's experimental plans in conducting an additional number of combustion runs when specific data was needed to be verified.
- Major improvements to the dilution ratio measurement and control procedures by using a CO₂ tracer technique demanded installation of additional control equipment on the sampling system and modification and verification of the software. The time required for these tasks was not included in the original plan. However, the time spent was well worth the benefits.

- The relatively long turnaround time for PM analysis procedures were unavoidable but highly undesirable. Some experiments could not proceed until the analytical data from previous experiments were known.
- CETC experienced several operational problems that are common to most laboratories. These include occasional malfunction of the emission analyzers, flue gas conditioning systems, fuel transfer pumps, humidification chamber, several general laboratory equipment and electronic control system failures on the fine PM measurement system. Long waiting periods involved in ordering supplies and equipment also added to the project delays.

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Table 1 - Identification of test fuels

Fuel ID	Fuel type	Sulphur content
LD-500	Low-sulphur diesel	560 ppm
LD-1000	Spiked diesel fuel	1000 ppm
LD-3000	Spiked diesel fuel	3000 ppm
LD-6000	Spiked diesel fuel	6000 ppm
No. 2	No. 2 heating fuel	1950 ppm
HF-R	No. 6 reference fuel	1.97 wt %
HF-0.7	No. 6 fuel oil (low-sulphur)	0.7 wt %
HF-1.7	No. 6 fuel oil (spiked high-sulphur)	1.7wt %
HF-2.3	No. 6 fuel oil (high-sulphur)	2.3 wt %
HF-3.5	No. 6 fuel oil (spiked high-sulphur)	3.5 wt %

Table 2 - Properties of light distillate fuels

Properties	LD-500	LD-1000	LD-3000	LD-6000	No. 2
Ultimate analysis (wt %)					
Carbon	87.60	86.63	86.55	86.05	86.68
Hydrogen	13.30	13.47	13.35	13.23	13.40
Nitrogen	0.04	0.05	0.05	0.04	0.07
Sulphur	0.06	0.10	0.31	0.62	0.20
Ash	0.00	<0.01	<0.01	NA	0.00
Density at 15°C (kg/m ³)	838.0	838.3	838.9	839.5	847.2
Gross calorific value (cal/g)	10885	10903	10896	10893	10823
Gross calorific value (MJ/kg)	46	46	46	46	45
Gross calorific value (Btu/lb)	19596	19628	19615	19610	19484
Kinematic viscosity at 40°C (cSt)	2.3	NA	NA	2.3	NA

Table 3 - Properties of heavy residual fuels

Properties	HF-2.3	HF-0.7	HF-R
Ultimate analysis (wt %)			
Carbon	86.16	87.03	87.44
Hydrogen	10.07	10.85	10.06
Nitrogen	0.43	0.28	0.38
Sulphur	2.28	0.70	1.97
Ash	0.00	0.00	0.04
Density at 15°C (kg/m ³)	979.8	947.1	996.9
Specific gravity at 60/60°F	0.9804	0.9477	0.9975
Gross calorific value (cal/g)	10111	10382	10136
Gross calorific value (MJ/kg)	42	43	42
Gross calorific value (Btu/lb)	18202	18690	18247
Kinematic viscosity at 100°C (cSt)	42.4	16.4	29.1

Table 4. Hydrocarbon Type Analysis of Different Fuels (wt%)

Hydrocarbon	LD-500	LD-1000	LD-3000	No. 2	HF-R	HF-0.7	HF-2.3
Saturates	70.8	70.9	70.5	64.8	25.0	43.1	24.0
Total Aromatics	29.2	29.1	29.5	35.2	42.5	36.3	45.7
Monoaromatics	21.6	21.4	21.8	24.5	ND	ND	ND
Diaromatics	6.8	6.9	6.9	9.2	ND	ND	ND
Polyaromatics	0.8	0.8	0.8	1.5	ND	ND	ND
Polars	NA	NA	NA	ND	15.9	17.9	18.4
Pentane Ashphatenes	NA	NA	NA	ND	16.6	2.7	12.0

NA: Not Available - Light distillate fuels do not contain such compounds.

ND: Not Determined - Incompatibility between fuel property and analytical technique.

Table 5 - Summary of laboratory procedures

No	DR	RH	S	Bacharach Smoke No.	Comments
1	42	40	-	-	Burner and dilution tunnel optimization.
2	-	-	-	-	Burner and dilution tunnel optimization.
3	-	-	-	-	Burner and dilution tunnel optimization. Problem with the sensor configuration on Boiler AB and CETC dilution tunnel.
4	-	-	-	-	Burner and dilution tunnel optimization.
5	46	40	1950	2	Dilution sampling run.
6	46	40	1950	2	Dilution sampling run.
7	-	-	1950	2	Dilution sampling run (PM loading).
8	-	-	-	-	Fuel mixing formula calculation and preparation.
9	-	-	-	-	Replaced the 6" stack with a 3" stack on the Utica Boiler.
10	-	-	-	2-	Utica Boiler optimization with 3" stack.
11	-	-	-	2	Reverted back to the 6" stack on the Utica Boiler.
12	-	-	-	-	Dilution tunnel cleaning and low-sulphur diesel fuel preparation.
13	-	-	-	-	Calibrated the relative humidity sensor on the CETC dilution tunnel.
14	-	-	-	2	Adjusted the boiler to conform with the original settings.
15	41	40	560	2	Cycling run. New CO ₂ analyzer installed along the required software changes.
16	41	31.2	560	2	Unstable dilution air controllers. Fluctuation in tunnel CO ₂ levels. Low dilution air pressure.
17	-	-	560	2	M5 PM loading run.
18	41	35.7	560	2-	Dilution sampling run.
19	-	-	-	-	6000 ppm low-sulphur diesel fuel preparation.
20	42	40	560	2	Dilution sampling run. Unstable stack draft. Drop in NO _x .
21	42	40	560	2	Dilution sampling run.
22	42	40	560	2	Dilution sampling run (SEM samples).
23	39	40	560	2	Dilution sampling run (PM loading and SEM samples).
24	39	40	560	2	Cycling run.
25	42	40	560	trace	Burner optimization run.
26		40	560	2	Dilution sampling run (PM loading run for 24 hrs).
27			560	2	Reverted back to the original burner settings from FQ-4 - FQ-7.
28	41	40	6000	2	Setup test. Switched fuels.
29	41	40	6000	2	Dilution sampling run (PM loading and SEM samples). CO ₂ level in flue gas declined.
30	-	-	-	-	Meeting to discuss the rotary kiln and No. 6 fuel delivery system modifications.
31	40	40	6000	2	Dilution sampling run. Run was shut down due to NO _x analyzer maintenance.
32	40	40	6000	2	Dilution sampling run (SEM samples).
33	40	40	6000	3	Dilution sampling run (PM loading). Smoke number was adjusted.
34	41	40	6000	2	Dilution sampling run (PM loading). CO ₂ analyzer spanning and zeroing problems.
35	41	40	6000	2	Dilution sampling run (SEM and OC/EC samples)
36	-	-	1000	-	Setup test. Switched fuels.
37	42	40	1000	2	Software setup test to automate tunnel CO ₂ control.
38	42	40	1000	2	Dilution sampling run (SEM samples and PM loading). O ₂ analyzer problem.
39	-	-	1000	1.5-2	Cycling run - unable to complete due to O ₂ analyzer problem.
40	45	40	1000	1.5-2	O ₂ analyzer not warmed up. Values not accurate.
41	45	40	1000	1.5-2	Dilution sampling run (SEM samples and PM loading). Pump fixed.
42	-	-	1000	1.5-2	Cleaned the probe and setup tunnel for cycling run. Prepared 3000 ppm fuel,
43	40	40	1000	1.5-2	Dilution sampling run (SEM samples).
44	40	40	1000	1.5-2	Dilution sampling run (OC/EC samples).
45	40	40	1000	1.5-2	Dilution sampling run (PM loading). Electrical failure.
46	-	-	-	1.5-2	Designed a fuel delivery system to be used on the rotary kiln.
47	-	-	-	1.5-2	Repairs were made to controller which had blown a fuse.
48	40	40	1000	1.5-2	Dilution sampling run.
49	40	40	1000	1.5-2	Dilution sampling run.

Table 5 - Summary of laboratory procedures (continued)

No	DR	RH	S	Bacharach Smoke No.	Comments
50	-	-	3000	1.5-2	Burner setup. Cleaned and collected losses from dilution tunnel and probe.
51	40	40	3000	1.5-2	Cycling run. Dilution sampling run (SEM samples and PM loading).
52	40	40	3000	1.5-2	Cycling run.
53	40	40	3000	1.5-2	Dilution sampling run (PM loading and SEM samples). CO ₂ level decreased and O ₂ increased after inserting probe.
54	40	40	3000	1.5-2	Cycling run. Dilution sampling run (SEM samples and OC/EC samples).
55	40	40	3000	1.5-2	Dilution sampling run (PM loading).
56	-	-	-	-	Moved the feed barrel from 2 nd floor to the ground level. Reduced the length of both the feed and return lines.
57	-	-	-	-	Replaced the small rotary pump with the larger mono pump.
58	-	-	No. 6	-	Fired-up the kiln with No. 6 fuel oil. Problems with flame stability.
59	-	-	No. 6	-	Replaced the nozzle on the fuel gun and installed a needle valve on the atomizing air line to stabilize air pressure.
60	39	40	560	1.5-2	Cycling run. Dilution sampling run (OC/EC samples). Power failure after 5.5 hrs, boiler restarted and test continued.
61	-	-	No. 6	-	M5 PM loading run. Unstable flame and insufficient PM loading on the M5 filter.
62	-	-	-	-	Disassembled dilution tunnel for cleaning and collected losses.
63	-	-	No. 6	-	Optimization of rotary kiln operation. Fuel line became clogged.
64	-	-	No. 6	-	Cleaned the entire fuel delivery system (nozzle, fuel gun, fuel lines, and valves) and installed filters on the fuel line.
65	-	-	No. 6	-	Improved the heating band setup on the feed barrel and utilized a rotary pump for transferring No. 6 fuel between barr Installed a pressure regulator and gauge on the air line along with a needle valve on the fuel line in order to control flame stability.
66	-	-	No. 6	-	Optimization of rotary kiln operation.
67	-	-	No. 6	-	Optimization of rotary kiln operation.
68	-	-	No. 6	1-6	M5 PM loading run. Excessive PM loading on the M5 filter and clogging of nozzle at the conclusion of the run.
69	-	-	No. 6	1-2	Optimization of rotary kiln operation.
70	-	-	No. 6	-	Installed a better needle valve on the fuel line and optimized the rotary kiln under these new conditions.
71	42	40	No. 2	1.5-2	Dilution sampling run (Mass loading).
72	44	40	No. 2	1.5-2	Dilution sampling run (Mass loading, SEM samples and OC/EC samples).
73	-	-	-	-	Disassembled dilution tunnel and moved to building #7 (rotary kiln).
74	-	-	-	-	Assembled dilution tunnel and associated units to be used with the rotary kiln.
75	-	-	No. 6	-	Replaced the existing scales with a digital system in order to monitor the firing rate.
76	-	-	-	-	Setup span gases and analyzers.
77	-	-	No. 6	1-2	M5 PM loading run. CETC dilution sampling run failed due to unsteady emissions.
78	-	-	No. 6	-	0.7 wt %, 1.7 wt %, 2.3 wt %, and 3.5 wt % Sulphur No. 6 fuel mixing formula calculation and preparation.
79	-	-	No. 6	-	Cleaned the nozzle and resolved the clogging issue.
80	-	-	No. 6	-	Installed heating tapes and controllers on the fuel line in order to stabilize fuel temperatures.
81	-	-	No. 6	1-2	Performed a series of three runs to optimize the kiln operations and finalized testing conditions in terms of emissions and operating parameters.
82	43	40	No. 6	2-9	Dilution sampling run on rotary kiln. Fluctuation in stack emissions and excessive particulate loading due to poor fuel combustion.
83	38	40	No. 6	1.5-2	Dilution sampling run on rotary kiln. Stable emissions with high levels of excess O ₂ .
84	-	-	No. 6	1.5-2	M5 PM loading run.
85	40	40	No. 6	1.5-2	Dilution sampling run on rotary kiln. Stable emissions with high levels of excess O ₂ .
86	-	-	-	-	Disassembled dilution tunnel for cleaning and collected losses.
87	-	-	No. 6	1-2	Dilution sampling run on rotary kiln. Unstable stack emissions.
88	-	-	-	-	Disassembled dilution tunnel for cleaning and collected losses.
89	-	-	-	-	Returned the dilution tunnel and associated units to building #1 for further tests on the Utica boiler.
90	-	-	-	-	Boiler setup. Switched fuels.
91	-	40	6000	1.5-2	Repeat dilution sampling run.

S: Sulphur concentration (ppm)

DR: Dilution ratio

RH: Relative humidity

Boiler: Utica Model No. SFH3100W (Serial No. HT11826)

Burner: Beckett high-efficiency model AFG (Serial No. 960513-50727)

Firing rate: 1.0 USGPH

Rotary kiln was used for No. 6 reference fuel oil combustion only.

Table 6. Comparison of combustion conditions for test fuels

	LD-500		LD-1000			LD-3000			LD-6000		
Test Room Temperature (°C)	19.0	19.6	19.7	20	20.5	20.1	21.2	20.1	19.6	20	20.6
Stack Temperature (°C)	220.0	218	224	229	227	233	232.5	232.8	209	219	218.9
Excess air & Efficiency											
Efficiency Losses:											
Dry flue Gas (%)	8.7	8.6	8.8	9	9.1	9.1	9.2	9.3	8.6	8.8	8.9
Fuel Hydrogen (%)	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.3	7.4	7.4
Radiation & Convection (%)	1	1	1	1	1	1	1	1	1	1	1
Efficiency (%)	83	83	83	83	82	82	82	82	83	83	83
Excess Air (%)	21	21	20	20	24	19	22	23	25	23	26
Dry Gas (lb./lb. Fuel)	17.21	17.25	17.14	17.17	17.64	17.09	17.41	17.55	17.88	17.56	17.87

Table 7. Gaseous emissions of test fuels during steady state and cyclic operation

		LD-500		LD-1000			LD-3000			LD-6000		
Test Room Temperature	°C	19	20	20	20	21	20	21	20	20	20	21
Stack Temperature	°C	220	218	224	229	227	233	233	233	209	219	219
Stack emissions at steady state												
Stack Carbon Dioxide	%	12.8	12.8	12.9	12.8	12.5	12.9	12.7	12.5	12.3	12.5	12.3
Stack Oxygen	%	3.5	3.8	3.7	4.0	3.9	3.6	3.8	3.9	4.1	4.0	3.8
Stack Sulphur Dioxide	ppm	26	26	50	46	50	156	155	155	305	310	315
Stack Nitrogen Oxides	ppm	99	98	111	110	114	108	117	117	100	103	103
Stack Carbon Monoxide	ppm	29	22	25	23	23	23	21	20	21	22	25
Stack emissions during cyclic operation												
Stack Carbon Dioxide	%	12.9	12.9	13.0	13.0	12.9	12.9	12.8	12.7	12.5	13.0	12.6
Stack Oxygen	%	3.4	3.6	3.5	3.7	3.6	3.4	3.5	3.6	4.0	3.4	3.5
Stack Sulphur Dioxide	ppm	27	26	50	NA	49	157	157	157	310	354	324
Stack Nitrogen Oxides	ppm	98	98	112	109	108	116	116	118	104	104	103
Stack Carbon Monoxide	ppm	35	26	32	27	27	25	23	22	26	35	34

NA - Not Available

Table 8. Steady state gaseous emissions after normalizing to 3% O₂ concentrations

		LD-500		LD-1000			LD-3000			LD-6000		
Test Room Temperature	°C	19.0	19.6	19.7	20	20.5	20.1	21.2	20.1	19.6	20	20.6
Stack Temperature	°C	220.0	218	224	229	227	233	232.5	232.8	209	219	218.9
Steady State Corrected 3% O₂												
Stack Carbon Dioxide	%	13.2	13.4	13.4	13.6	13.1	13.3	13.2	13.2	13.1	13.3	12.9
Stack Oxygen	%	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Stack Sulphur Dioxide	ppm	27	27	52	49	52	161	162	163	325	328	330
Stack Nitrogen Oxides	ppm	101	102	116	116	120	112	122	123	107	109	108
Stack Carbon Monoxide	ppm	30	23	26	24	24	24	22	21	22	23	26

Table 9 - Filterable PM mass concentrations of test fuels

Fuel ID	Run	PM_{2.5} (mg/m ³)	PM₁₀ (mg/m ³)	PM_{Total} (mg/m ³)
LD-500	1	1.61	1.75	1.85
		1.74	1.92	
	2	2.08	2.41	2.34
		2.25	2.26	
	3	1.87	2.01	2.08
		2.00	2.19	
AVG		1.93	2.09	2.09
RSD (%)		12.06	11.65	11.58
LD-1000	1	3.61	3.50	3.62
		3.50	3.78	
	2	2.95	2.90	3.10
		2.88	3.17	
	3	3.50	3.19	3.17
		3.29	3.56	
AVG		3.29	3.35	3.29
RSD (%)		9.43	9.63	8.56
No.2	1	9.38	8.99	9.31
		9.28	9.82	
	2	10.27	9.88	10.28
		10.10	10.72	
	AVG		9.76	9.86
RSD (%)		5.10	7.18	7.01
LD-3000	1	13.24	12.64	12.58
		12.91	13.21	
	2	14.83	14.13	14.59
		14.37	15.28	
	3	14.22	13.40	14.45
		14.97	13.56	
AVG		14.09	13.70	13.87
RSD (%)		5.97	6.66	8.09
LD-6000	1	24.66	19.15	24.80
		19.94	26.73	
	2	21.53	22.40	24.42
		23.11	24.39	
	3	23.19	24.20	25.47
		24.40	26.21	
	4	25.41	24.39	25.54
		24.64	25.94	
AVG		23.36	24.17	25.06
RSD (%)		7.89	10.17	2.15

RSD(%)-Relative Standard Deviation

Table 10 - Trace element concentrations of PM for all fuels (%)

Fuel ID	Run	PM size	Si	P	S	Fe	Sn
LD-500	1	PM _{2.5}	0.17	0.46	3.43	0.03	0.11
		PM ₁₀	0.00	0.36	3.77	0.03	0.12
		PM _{Total}					
	2	PM _{2.5}	0.31	0.40	2.21	0.01	0.06
		PM ₁₀	0.04	0.21	2.33	0.02	0.07
		PM _{Total}					
3	PM _{2.5}	0.12	0.31	2.35	0.03	0.15	
	PM ₁₀	0.17	0.33	2.44	0.04	0.12	
	PM _{Total}	0.05	0.20	2.50	0.02	0.12	
LD-1000	1	PM _{2.5}	0.16	0.07	1.28	0.02	0.09
		PM ₁₀	0.00	0.14	1.42	0.02	0.08
		PM _{Total}	0.12	0.09	1.32	0.02	0.09
	2	PM _{2.5}	0.00	0.00	1.46	0.03	0.12
		PM ₁₀	0.08	0.00	1.62	0.00	0.12
		PM _{Total}	0.10	0.27	1.82	0.05	0.11
	3	PM _{2.5}	0.00	0.12	1.80	0.02	0.07
		PM ₁₀	0.07	0.19	1.87	0.03	0.08
		PM _{Total}	0.03	0.21	3.04	0.06	0.14
No.2	1	PM _{2.5}	0.00	0.12	2.34	0.00	0.03
		PM ₁₀	0.00	0.12	2.28	0.01	0.03
		PM _{Total}	0.08	0.18	1.93	0.00	0.03
	2	PM _{2.5}	0.00	0.12	1.78	0.04	0.31
		PM ₁₀	0.00	0.20	2.02	0.01	0.23
		PM _{Total}	0.00	0.00	1.51	0.02	0.43
LD-3000	1	PM _{2.5}	0.04	0.00	0.66	0.02	0.03
		PM ₁₀	0.12	0.04	0.73	0.02	0.03
		PM _{Total}	0.03	0.12	1.86	0.01	0.03
	2	PM _{2.5}	0.05	0.11	1.71	0.01	0.03
		PM ₁₀	0.00	0.07	1.56	0.00	0.03
		PM _{Total}	0.00	0.09	1.56	0.01	0.02
	3	PM _{2.5}	0.00	0.02	0.99	0.01	0.06
		PM ₁₀	0.00	0.08	1.04	0.03	0.05
		PM _{Total}	0.00	0.03	1.04	0.01	0.08
LD-6000	1	PM _{2.5}	0.01	0.01	0.71	0.00	0.02
		PM ₁₀	0.00	0.04	0.91	0.01	0.03
		PM _{Total}	0.00	0.02	0.56	0.00	0.02
	2	PM _{2.5}	0.00	0.00	0.00	0.00	0.03
		PM ₁₀	0.00	0.00	0.61	0.00	0.04
		PM _{Total}	0.12	0.00	0.00	0.00	0.03
	3	PM _{2.5}	0.00	0.09	0.58	0.01	0.03
		PM ₁₀	0.00	0.03	0.60	0.00	0.03
		PM _{Total}	0.04	0.22	0.69	0.02	0.02

Table 11 - Sulphate concentrations of PM for all fuels

Fuel ID	Run	PM size	SO ₄ (mg)	SO ₄ (%)	pH	Water of hydration (mg)
LD-500	1	PM _{Total}	297	24	NA	60
		PM _{Total}	346	21	NA	71
	2	PM _{Total}	263	18	NA	54
		PM _{Total}	314	18	NA	64
	3	PM _{2.5}	323	25	NA	66
		PM ₁₀	290	21	NA	59
LD-1000	1	PM _{2.5}	661	33	NA	135
		PM ₁₀	684	32	NA	140
		PM _{Total}	680	31	NA	139
	2	PM _{2.5}	378	32	2	77
		PM ₁₀	404	31	2	82
		PM _{Total}	494	30	2	101
	3	PM _{2.5}	568	38	2	116
		PM ₁₀	609	38	2	124
		PM _{Total}	571	40	2	116
No. 2	1	PM _{2.5}	1132	42	2	231
		PM ₁₀	1185	41	2	242
		PM _{Total}	1154	40	2	235
	2	PM _{2.5}	581	38	2	119
		PM ₁₀	605	37	2	123
		PM _{Total}	446	35	3	91
LD-3000	1	PM _{2.5}	1353	44	2	276
		PM ₁₀	1403	46	2	286
		PM _{Total}	1500	45	2	306
	2	PM _{2.5}	1413	43	2	288
		PM ₁₀	1465	42	2	299
		PM _{Total}	1540	42	2	314
	3	PM _{2.5}	778	43	2	159
		PM ₁₀	829	53	2	169
		PM _{Total}	802	41	2	164

Table 11 - Sulphate concentrations of PM for all fuels (continued)

Fuel ID	Run	PM Size	SO ₄ (mg)	SO ₄ (%)	pH	Water of Hydration (mg)
LD-6000	1	PM _{2.5}	3914	49	NA	798
		PM ₁₀	4078	38	NA	832
		PM _{Total}	4874	41	NA	994
	2	PM _{2.5}	651	46	NA	133
		PM ₁₀	680	46	NA	139
		PM _{Total}	814	43	NA	166
	3	PM _{2.5}	603	41	NA	123
		PM ₁₀	638	41	NA	130
		PM _{Total}	730	39	NA	149
	4	PM _{2.5}	633	44	4	129
		PM _{2.5}	612	44	4	125
		PM ₁₀	608	44	4	124
		PM ₁₀	650	44	4	133
		PM _{Total}	618	43	4	126

NA - Not Available

Table 12 - Carbon species concentrations of PM for all fuels

Fuel ID	Run	PM Fraction	Carbon						
			Organic		Elemental		Total		
			%	± (%)	%	± (%)	%	± (%)	
LD-500	1	PM _{2.5}	23.46	2.35	49.45	3.67	72.91	5.41	
			19.43	2.10	46.71	3.44	66.18	5.00	
		PM ₁₀	20.40	2.12	44.18	3.29	64.59	4.84	
			19.41	2.01	47.38	3.44	66.80	4.91	
		PM _{Total}	19.10	2.04	46.10	3.36	65.20	4.85	
LD-1000	1	PM _{2.5}	14.00	1.46	11.48	1.33	25.48	2.41	
			13.05	1.44	11.76	1.38	24.81	2.43	
		PM ₁₀	12.95	1.45	11.48	1.37	24.43	2.42	
			12.25	1.34	11.68	1.31	23.93	2.29	
		PM _{Total}	13.51	1.45	12.13	1.38	25.65	2.44	
No.2	1	PM _{2.5}	8.27	0.87	6.73	0.80	15.00	1.43	
			6.82	0.80	6.44	0.79	13.26	1.35	
		PM ₁₀	7.34	0.85	6.98	0.83	14.30	1.43	
			6.39	0.76	7.02	0.78	13.43	1.33	
			PM _{Total}	5.93	0.75	7.31	0.82	13.26	1.35
	2	PM _{2.5}	7.75	1.06	7.64	1.06	15.39	1.79	
			8.87	1.13	7.38	1.07	16.28	1.85	
		PM ₁₀	9.91	1.21	7.88	1.10	17.79	1.94	
8.58			1.09	7.75	1.04	16.34	1.79		
		PM _{Total}	8.28	1.08	8.28	1.08	16.56	1.84	
LD-3000	1	PM _{2.5}	4.75	0.82	0.84	0.63	5.57	1.16	
			8.10	0.98	0.75	0.63	8.83	1.33	
		PM ₁₀	5.03	0.86	0.76	0.66	5.81	1.23	
			4.93	0.84	0.94	0.63	5.87	1.17	
		PM _{Total}	6.66	0.92	0.83	0.64	7.52	1.28	
LD-6000	1	PM _{2.5}	11.67	1.59	5.16	1.27	16.83	2.35	
			9.39	1.51	5.50	1.32	14.89	2.31	
		PM ₁₀	7.81	1.39	5.33	1.27	13.14	2.16	
			8.76	1.35	6.26	1.22	15.02	2.11	
			PM _{Total}	6.03	1.24	5.56	1.22	11.58	1.99
	2	*PM _{2.5}	12.11	1.69	0.78	1.13	12.88	2.28	
			11.33	1.69	1.04	1.17	12.37	2.30	
		*PM ₁₀	12.12	1.74	0.74	1.17	12.87	2.34	
12.36			1.68	0.61	1.10	12.97	2.25		
		*PM _{Total}	9.95	1.58	0.96	1.13	10.91	2.17	

*Repeat run using LD-6000

Table 13 - PM mass balance results for test fuel (mg/m³)

Fuel ID	Species	PM _{2.5}	PM ₁₀	PM _{Total}	M5
LD-500	Metal as oxides	0.03	0.02	0.02	NA
	Organic carbon	0.71	0.71	0.68	NA
	Elemental carbon	1.00	1.03	1.03	NA
	Sulphur as sulphate & hydration	0.57	0.51	0.51	NA
	By composition analysis	2.31	2.27	2.24	NA
	By gravimetry	1.93	2.09	2.09	1.77
LD-1000	Metal as oxides	0.03	0.03	0.04	NA
	Organic carbon	0.71	0.67	0.71	NA
	Elemental carbon	0.38	0.39	0.40	NA
	Sulphur as sulphate & hydration	1.33	1.41	1.51	NA
	By composition analysis	2.45	2.50	2.66	NA
	By gravimetry	3.29	3.35	3.29	NA
No.2	Metal as oxides	0.10	0.09	0.09	NA
	Organic carbon	1.24	1.27	1.12	NA
	Elemental carbon	0.69	0.73	0.76	NA
	Sulphur as sulphate & hydration	4.69	4.90	ND	NA
	By composition analysis	6.72	6.99	ND	NA
	By gravimetry	9.76	9.86	9.80	NA
LD-3000	Metal as oxides	0.06	0.07	0.06	NA
	Organic carbon	1.44	1.09	1.48	NA
	Elemental carbon	0.11	0.12	0.11	NA
	Sulphur as sulphate & hydration	7.36	7.71	ND	NA
	By composition analysis	8.97	8.99	ND	NA
	By gravimetry	14.09	13.70	13.87	NA
LD-6000	Metal as oxides	0.08	0.70	0.15	NA
	Organic carbon	4.64	4.87	4.02	NA
	Elemental carbon	0.22	0.17	0.24	NA
	Sulphur as sulphate & hydration	12.20	12.78	13.10	NA
	By composition analysis	17.14	18.52	17.51	NA
	By gravimetry	23.31	24.13	25.00	NA

NA - Not Available

ND - Not Determined

Table 14 - Typical PM source profile for LD-1000 test fuel

Species		PM_{2.5}	±	PM₁₀	±	PM_{Total}	±
SO₄	(%)	34.40	1.72	33.58	1.68	33.53	1.68
H₂O	(%)	7.00	0.35	6.85	0.34	6.85	0.34
OC	(%)	13.50	1.45	12.65	1.35	13.50	1.40
EC	(%)	11.65	1.35	11.60	1.35	12.10	1.40
S	(%)	1.38	NA	1.54	NA	1.78	NA
Si	(ppm)	1125.00	NA	350.00	NA	625.00	NA
P	(ppm)	575.00	NA	1275.00	NA	1725.00	NA
Fe	(ppm)	200.00	NA	225.00	NA	425.00	NA
Sn	(ppm)	1075.00	NA	1050.00	NA	1150.00	NA

NA - Not Available

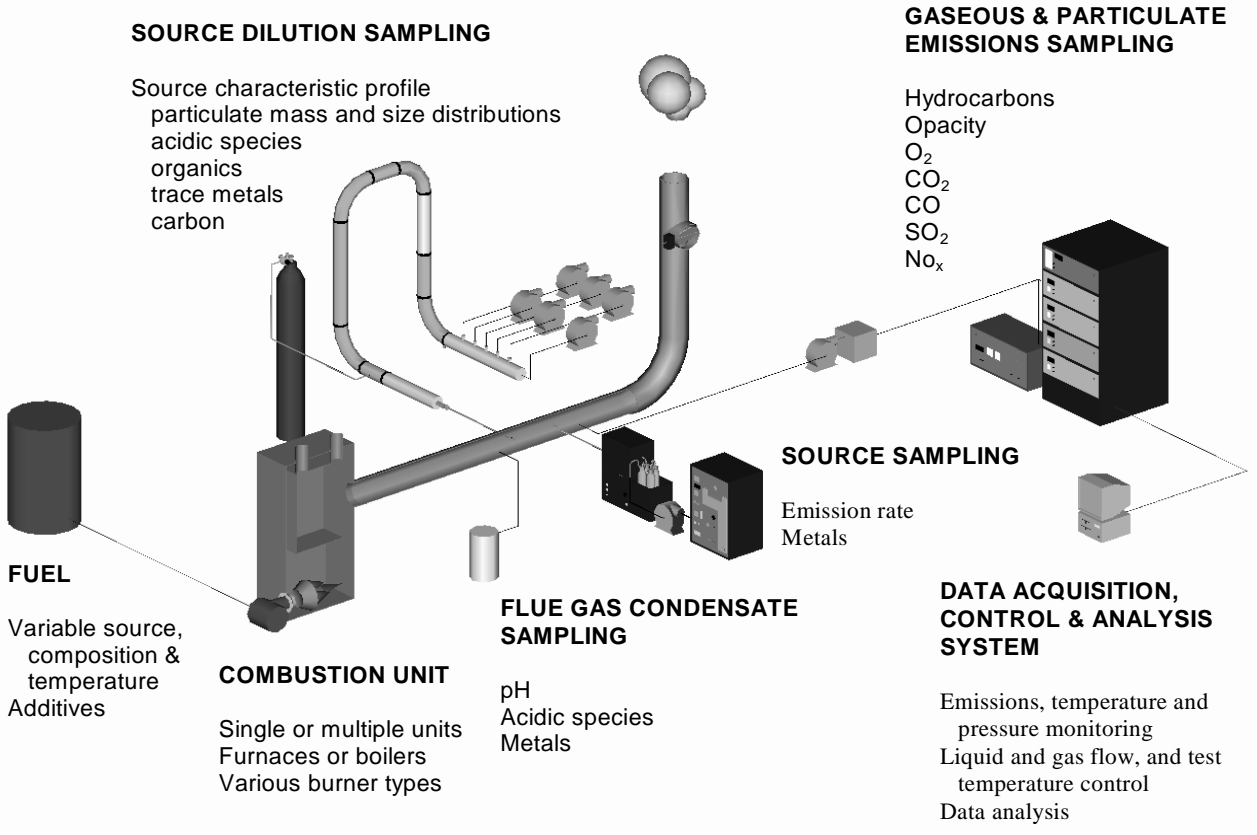


Figure 1 - Liquid fuel combustion research facilities

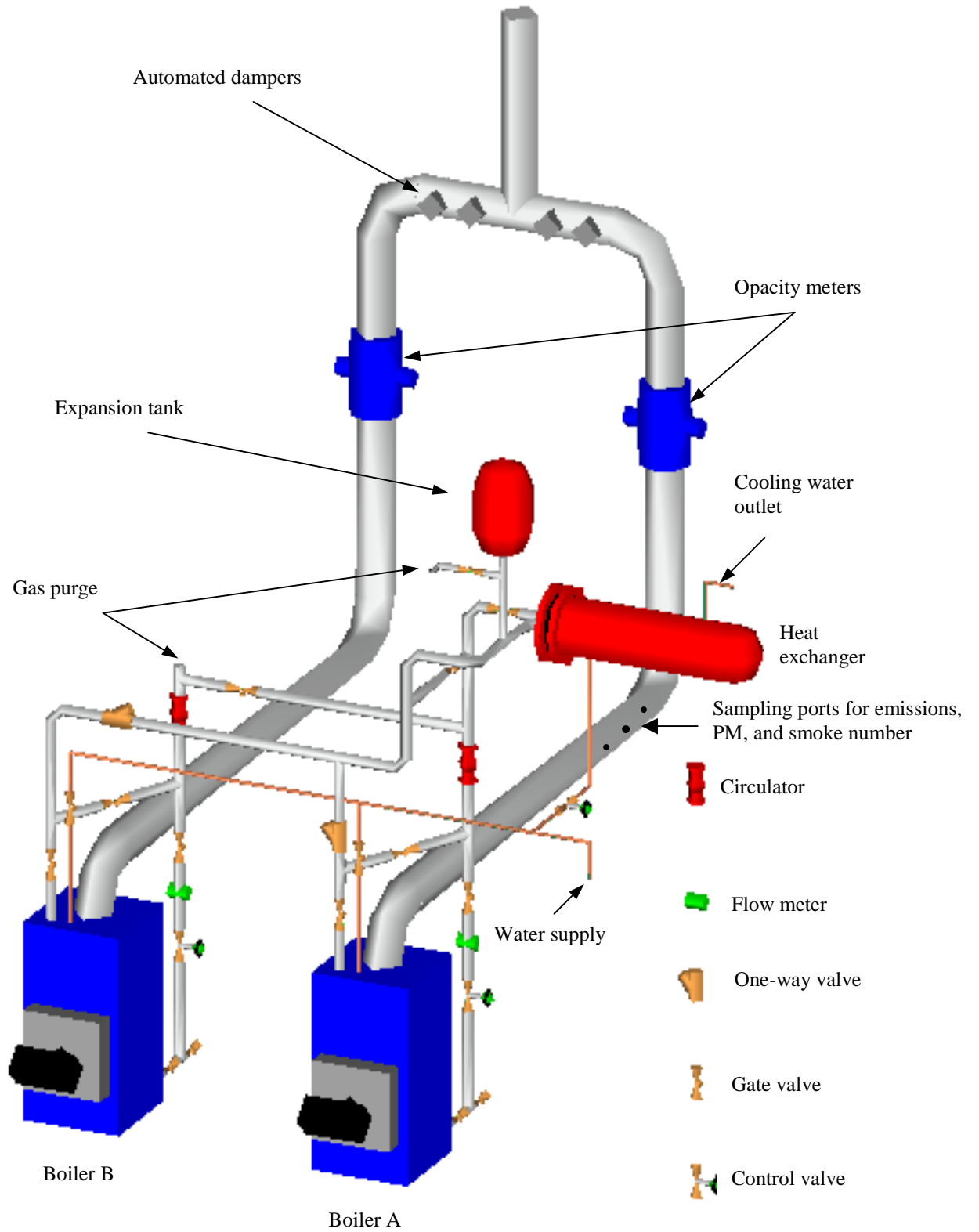


Figure 2 - Residential oil combustion laboratory test rig

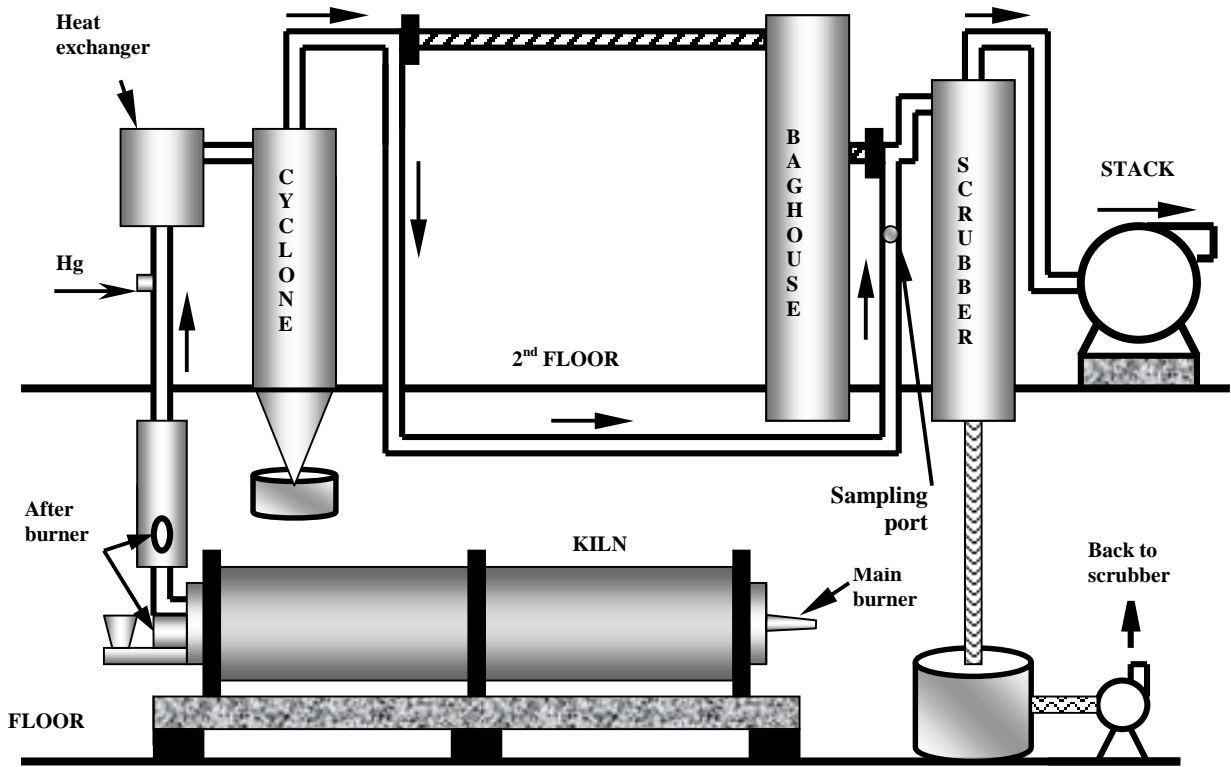


Figure 3 - Schematic of CETC rotary kiln facility

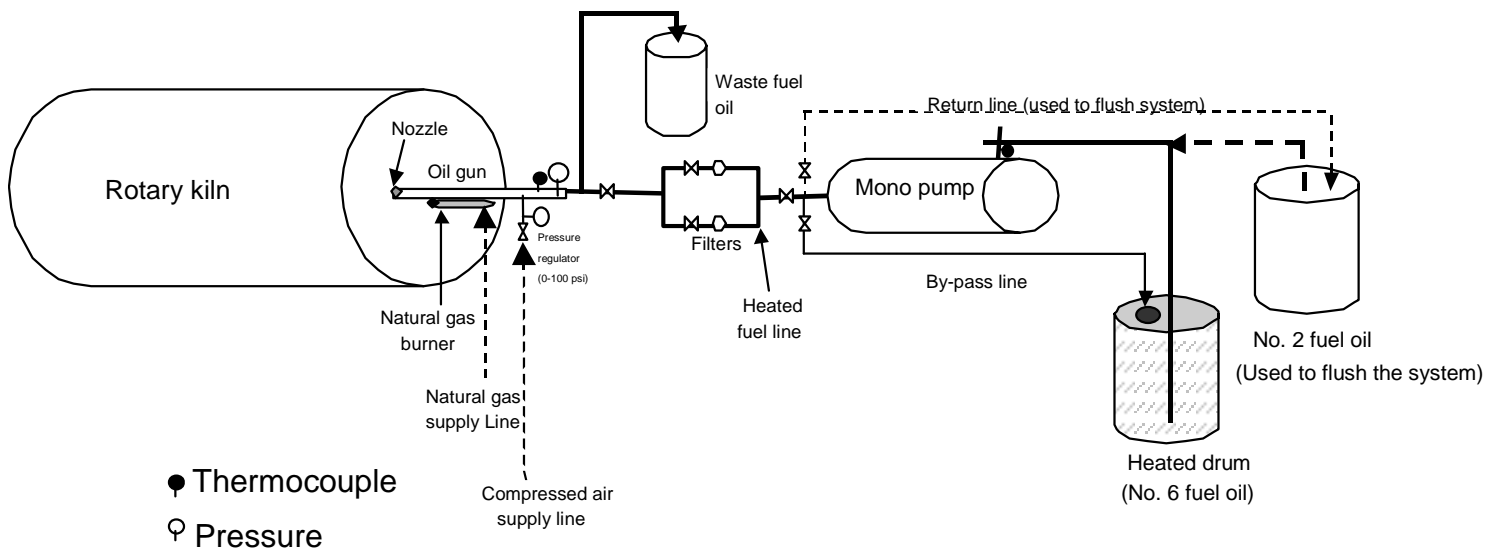


Figure 4 - Schematic of heavy fuel conditioning and delivery system for the kiln furnace

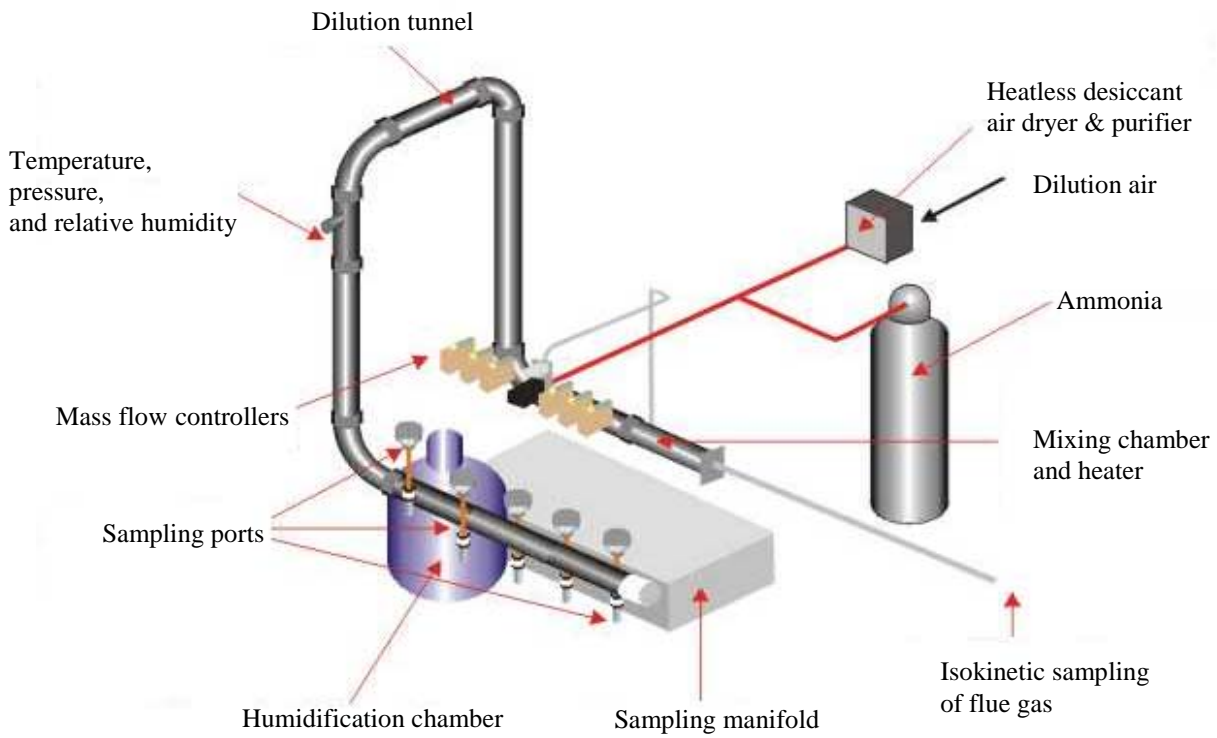


Figure 5 - CETC low-volume fine PM measurement system

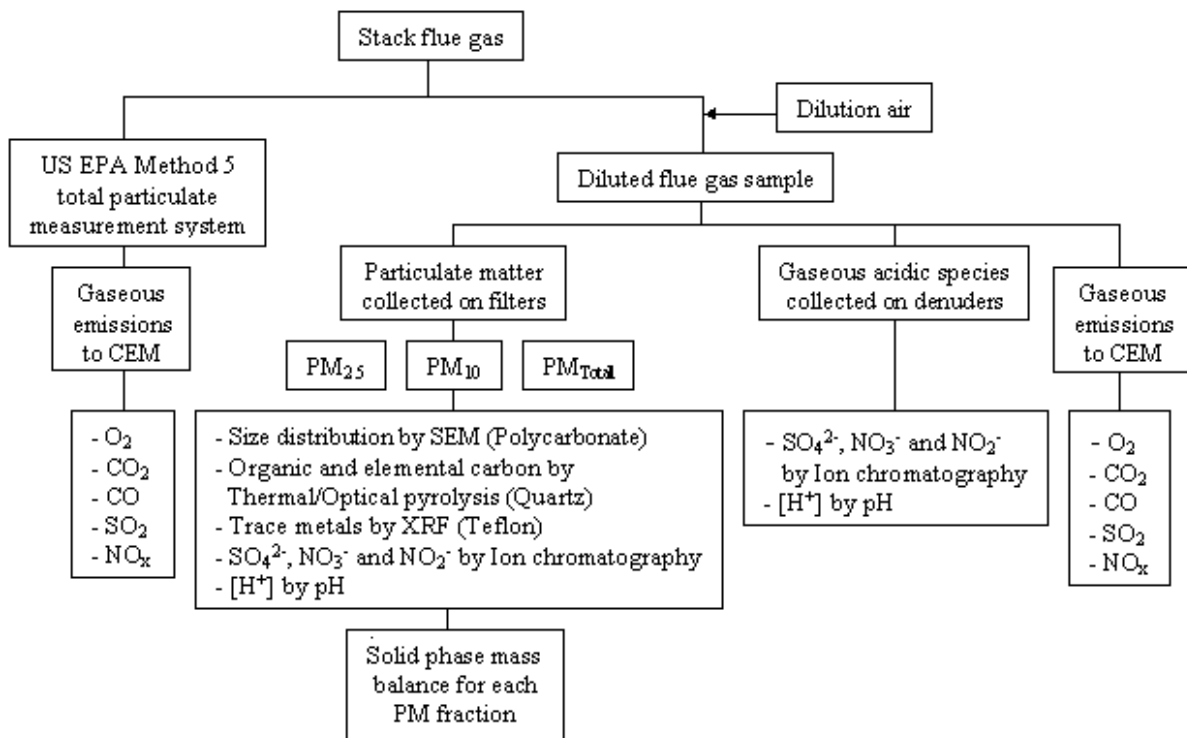
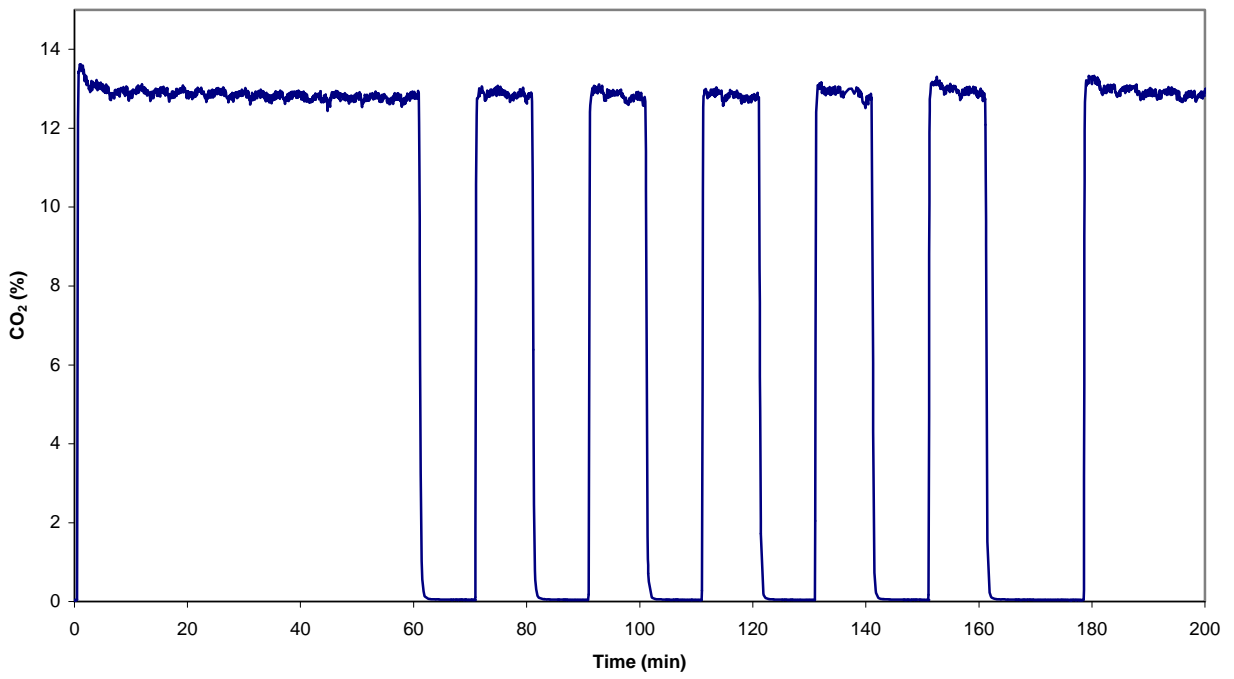
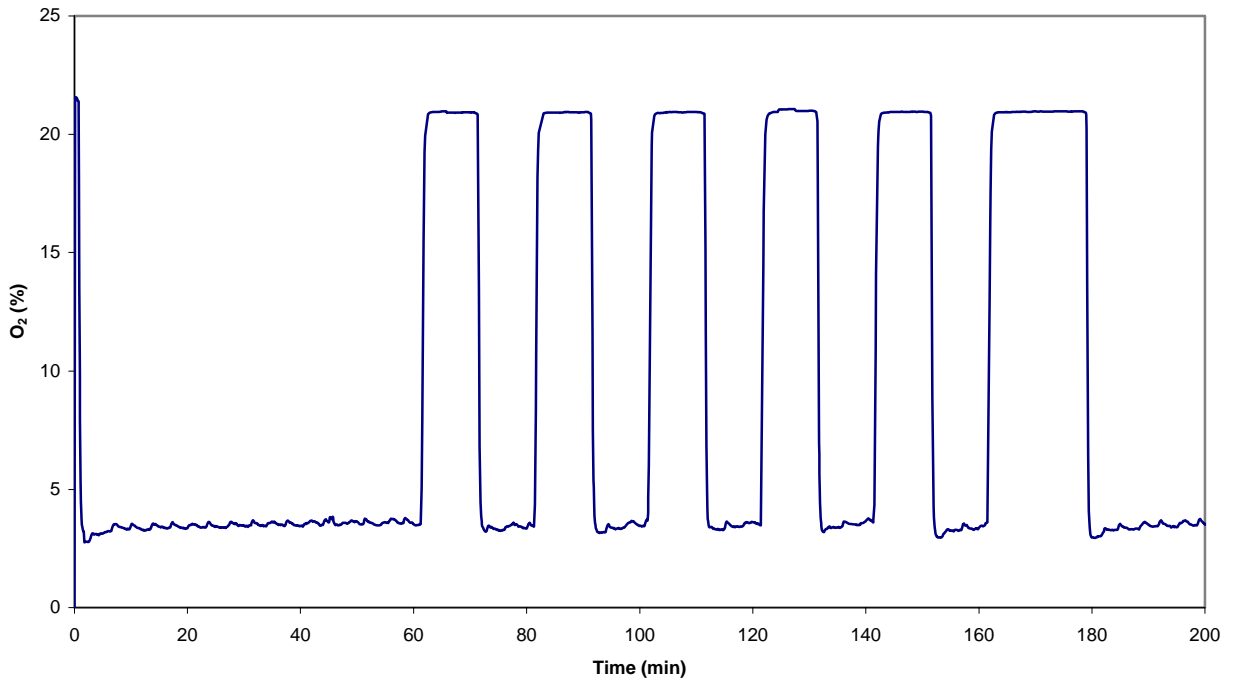
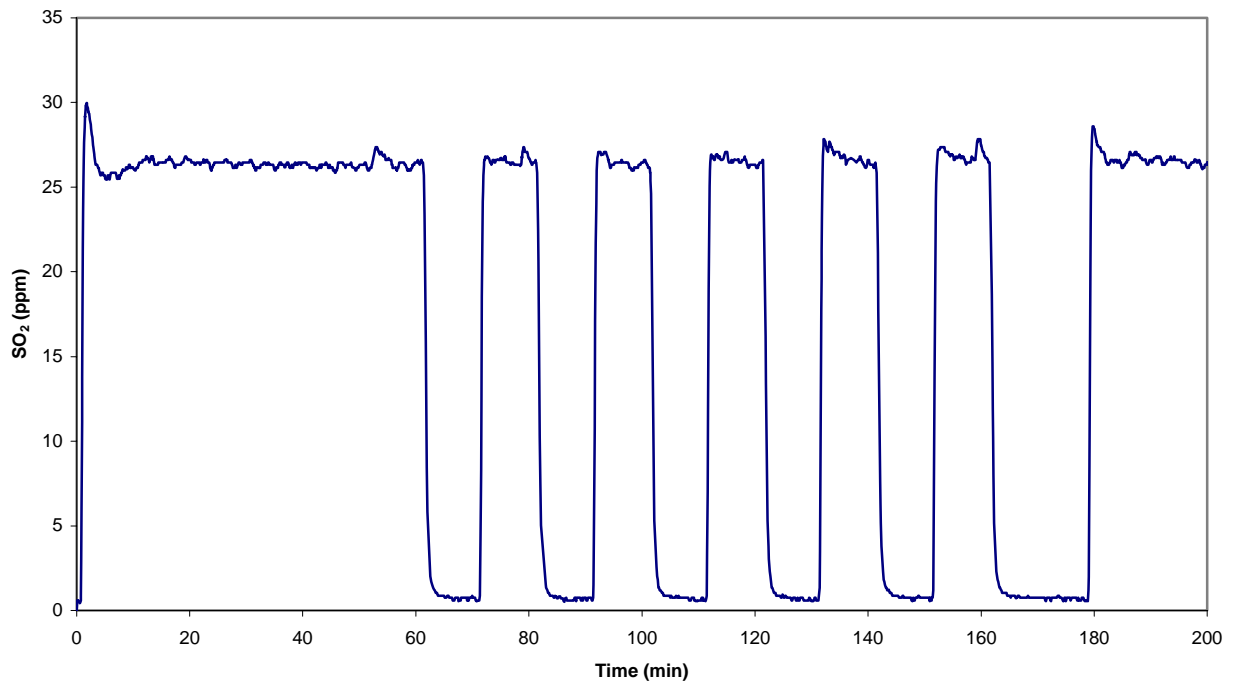
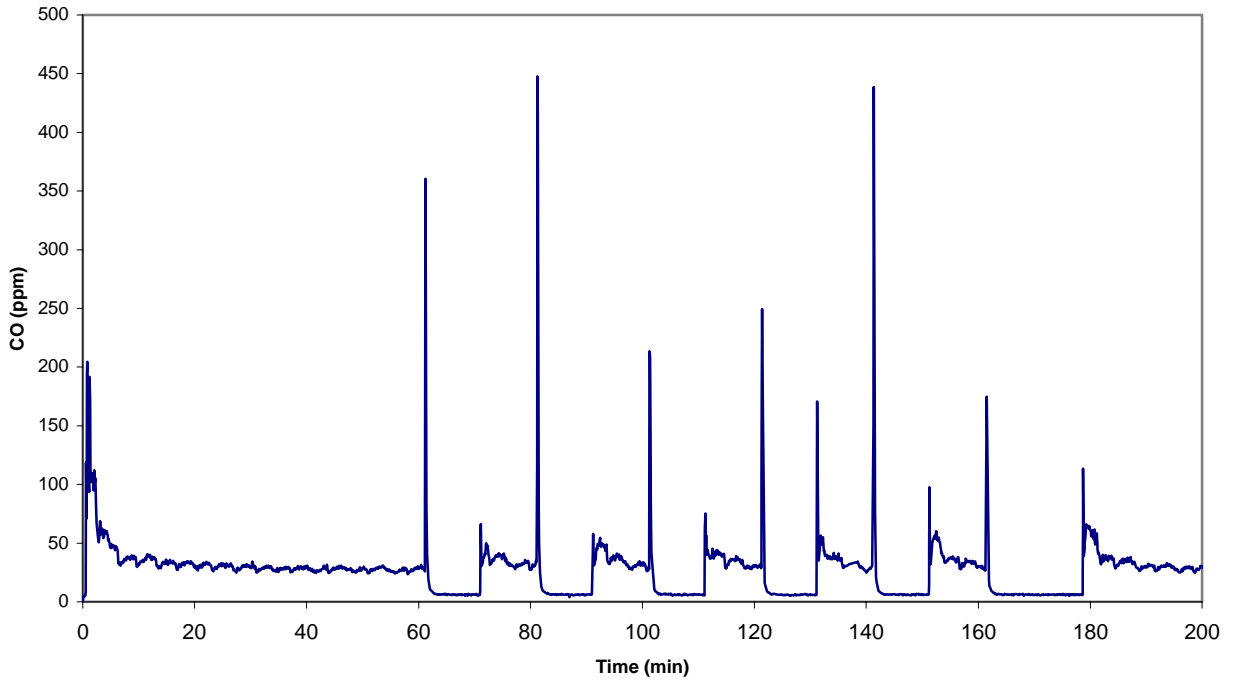


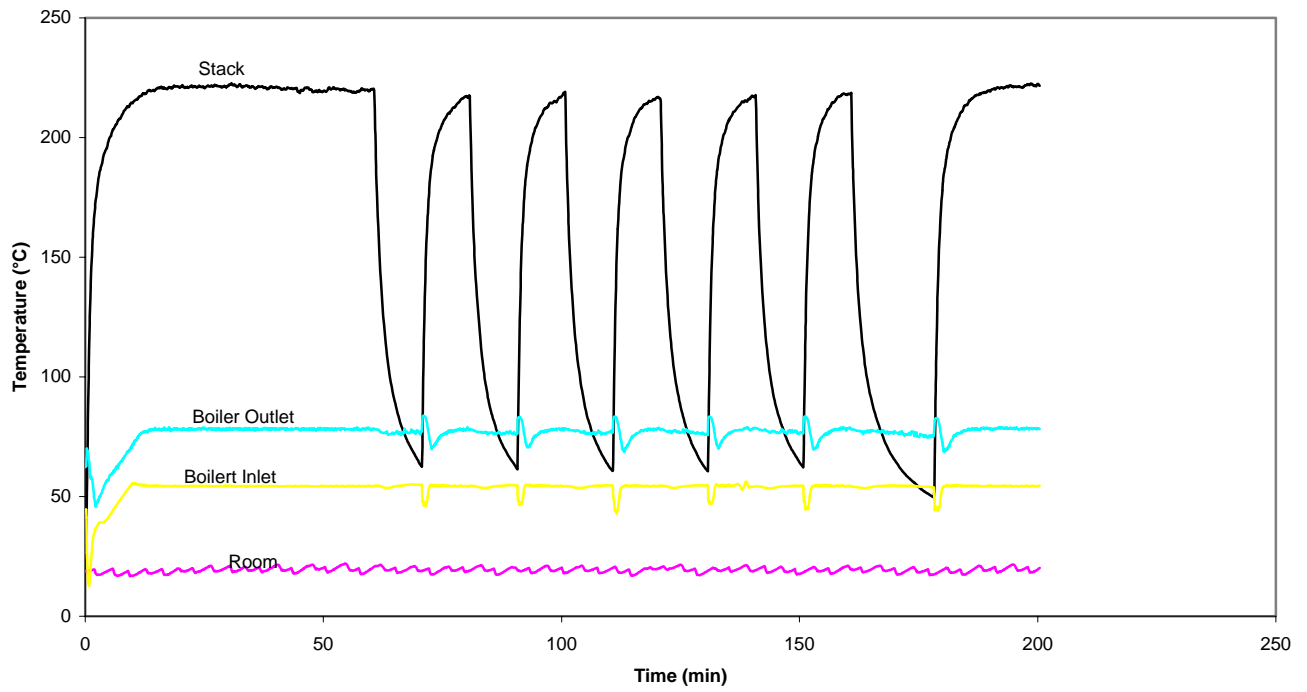
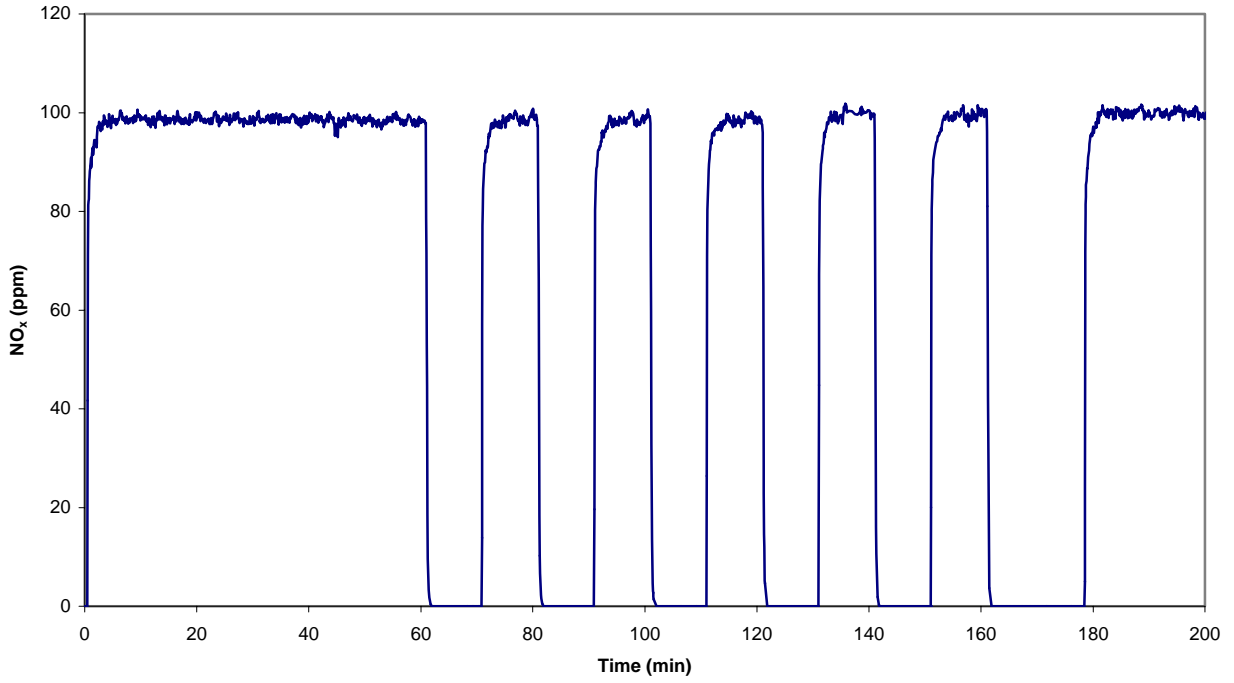
Figure 6 - PM sampling and analysis scheme

Figure 7 - Emission and temperature profiles from a combustion experiment using LD-500 fuel

- (a) Oxygen concentration**
- (b) Carbon dioxide concentration**
- (c) Carbon monoxide concentration**
- (d) Sulphur dioxide concentration**
- (e) Nitrogen oxide concentration**
- (f) Stack, boiler and room temperature profiles**
- (g) Stack draft and draft over flame**







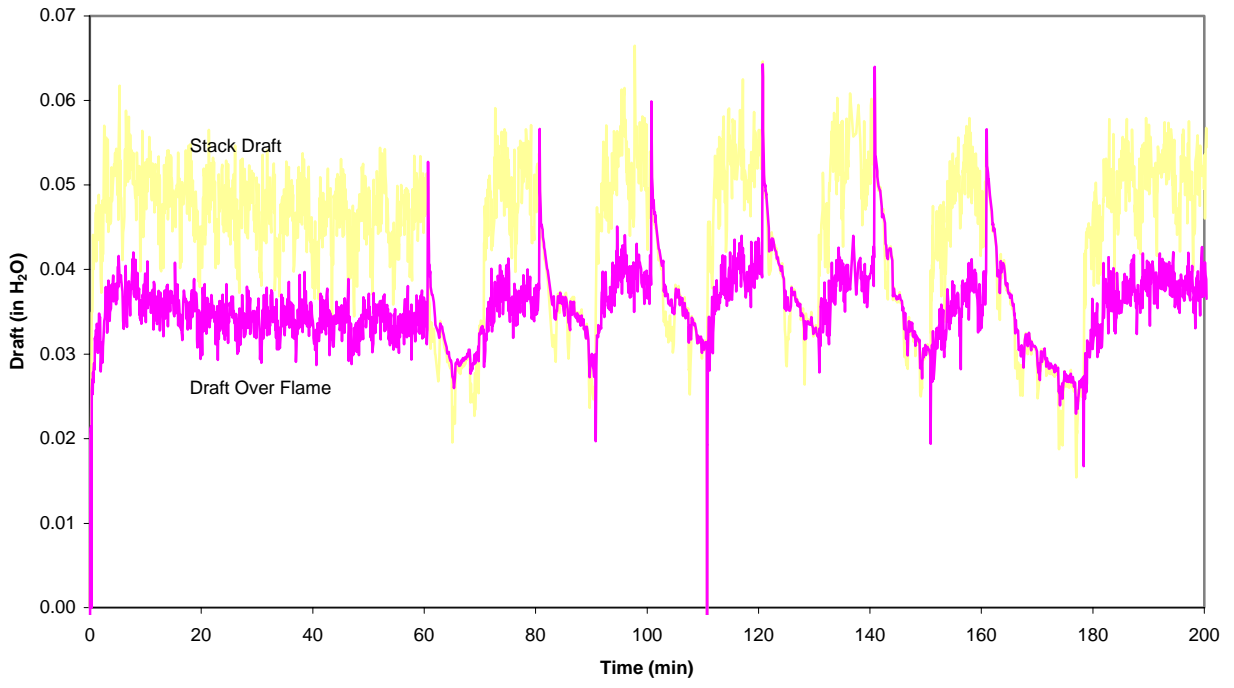
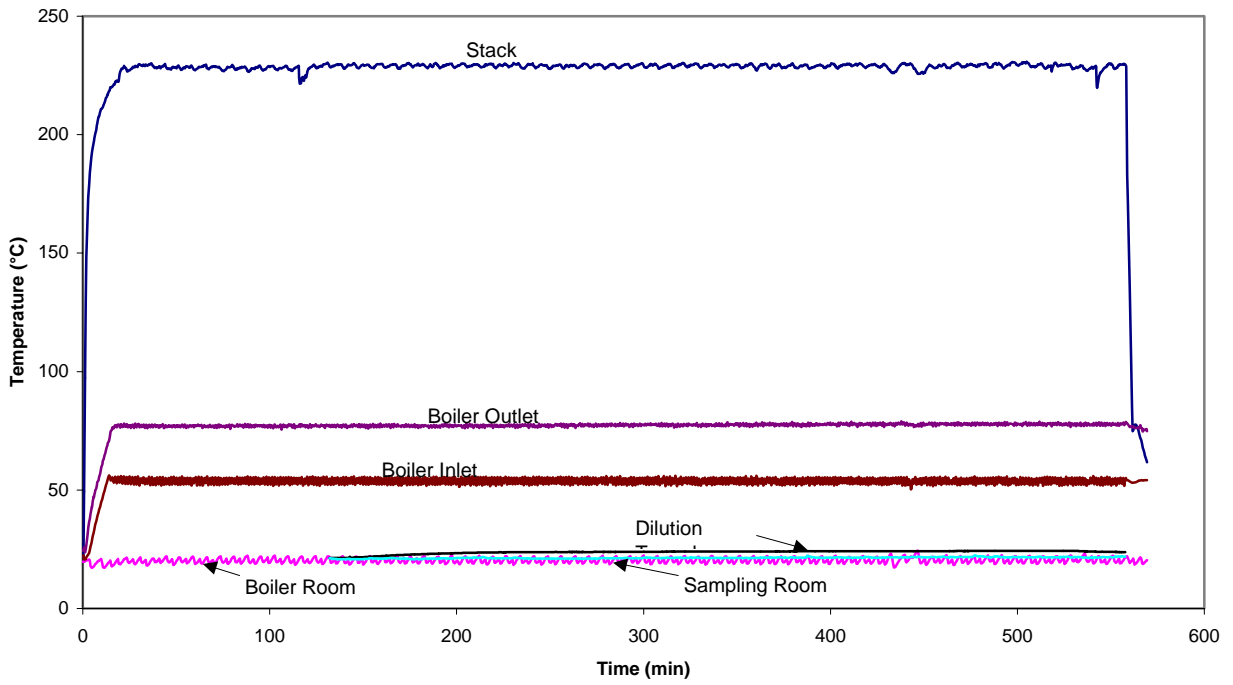
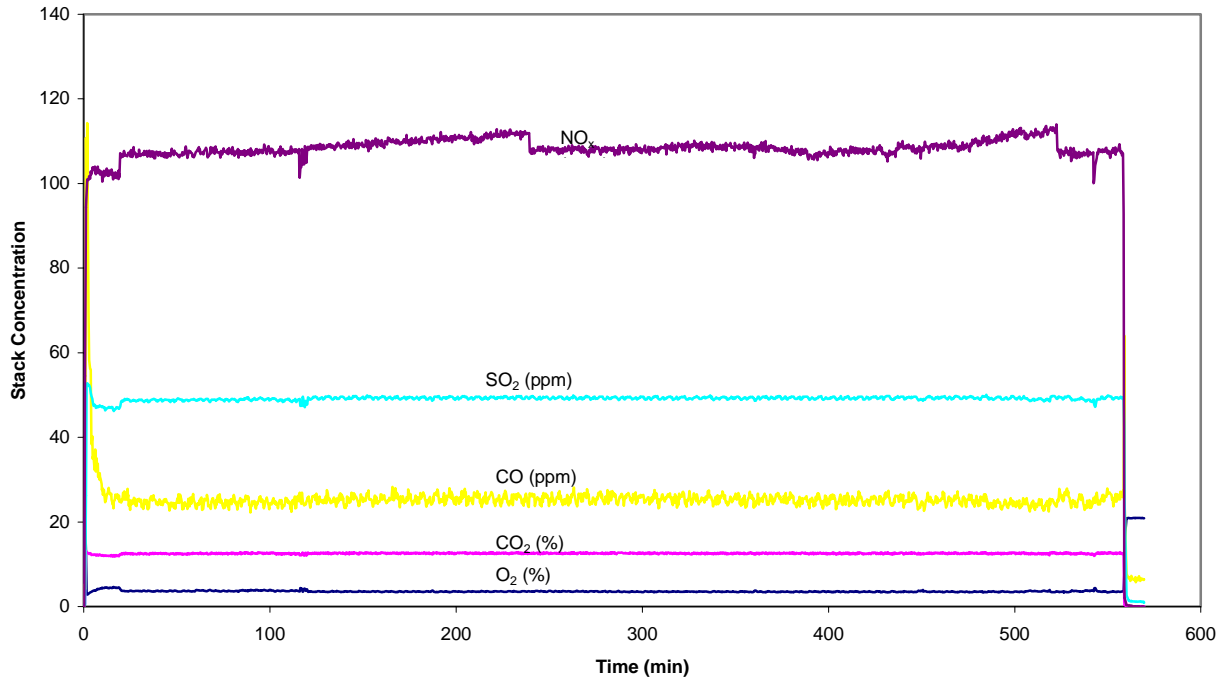
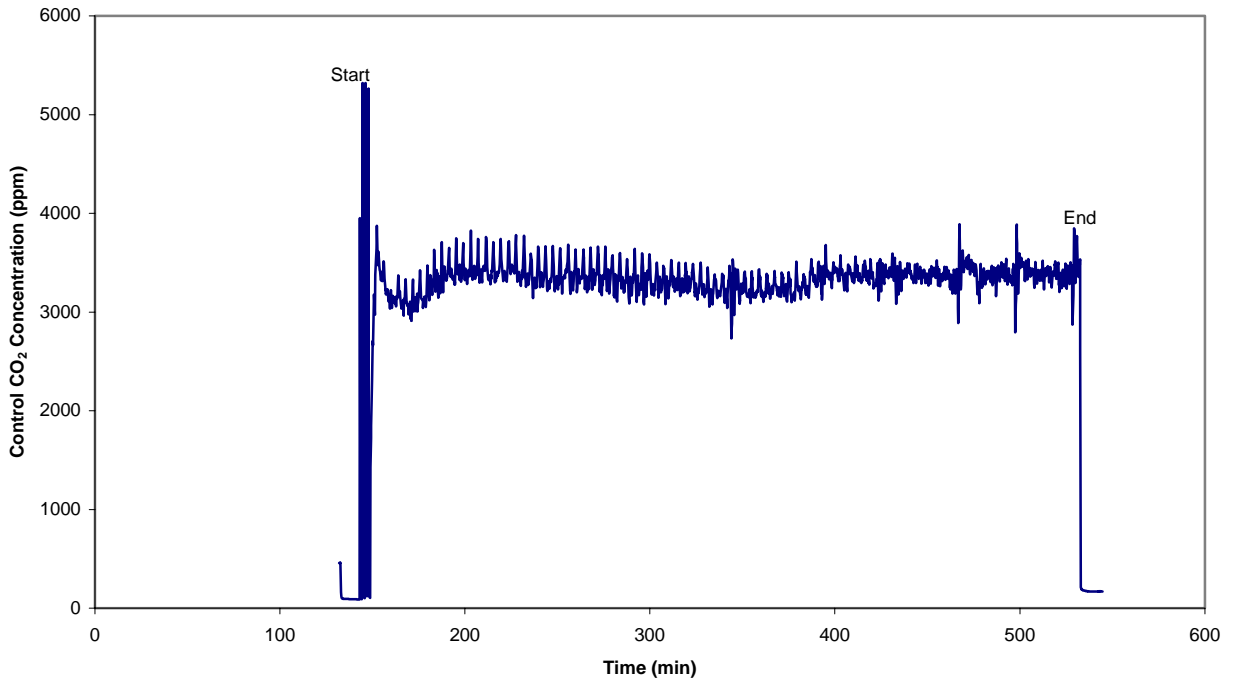
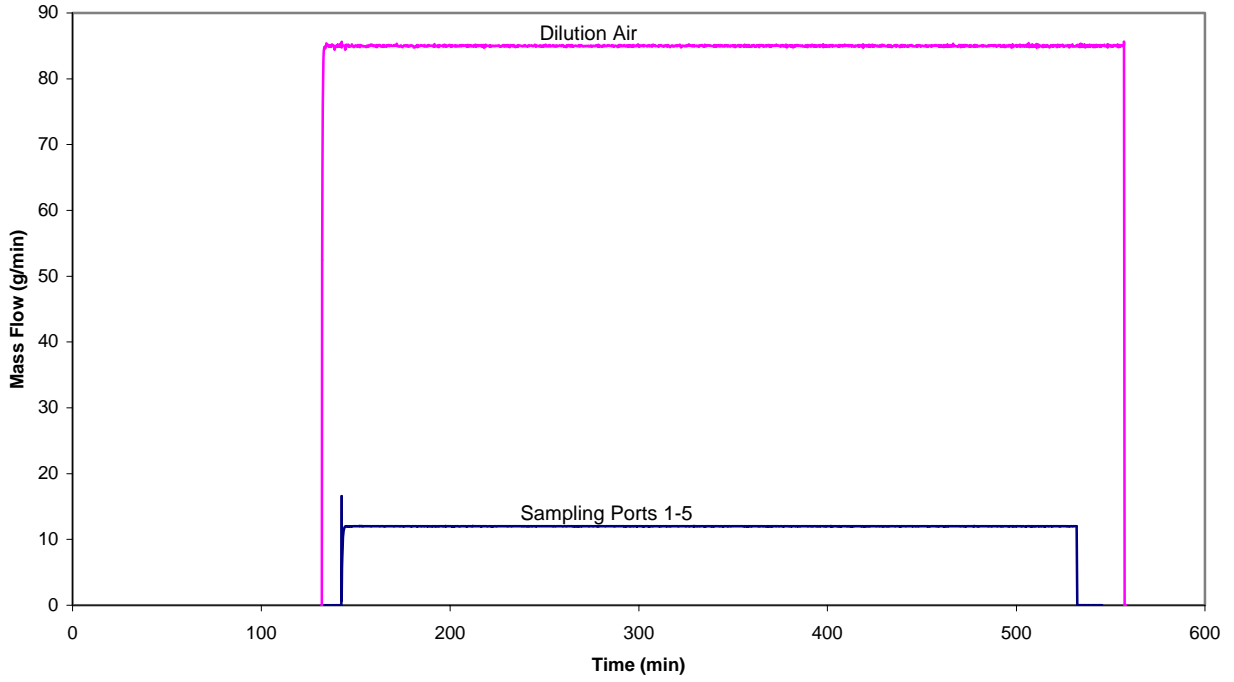
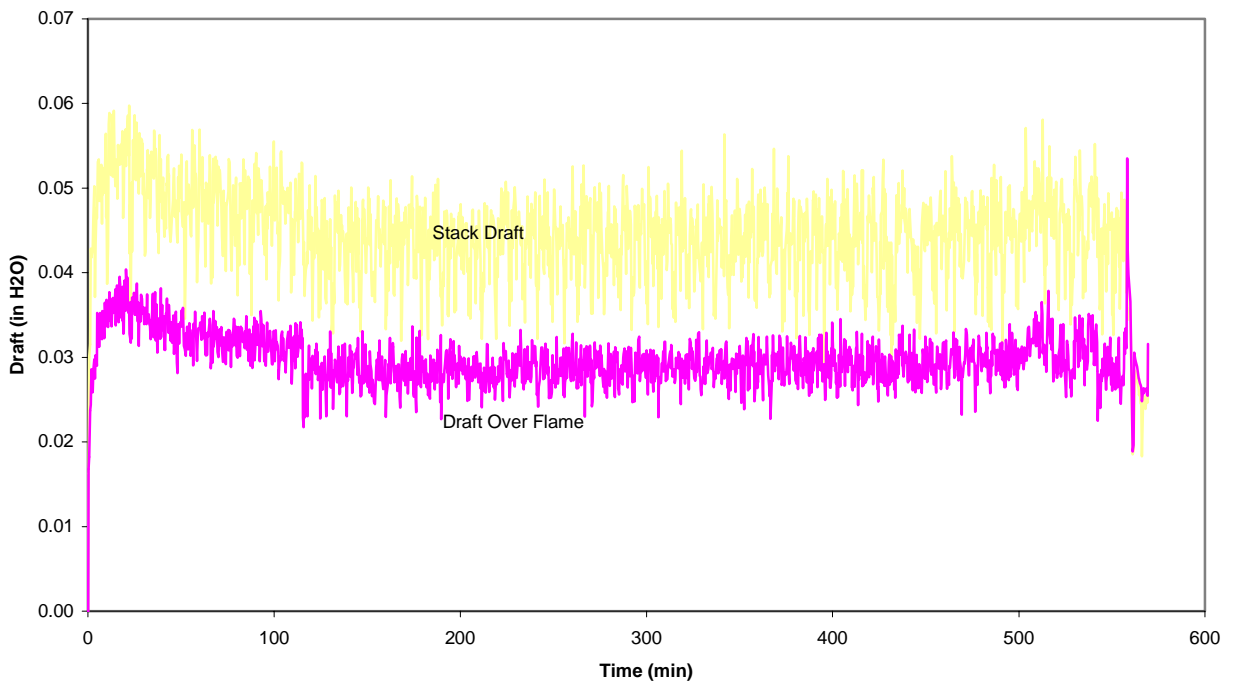
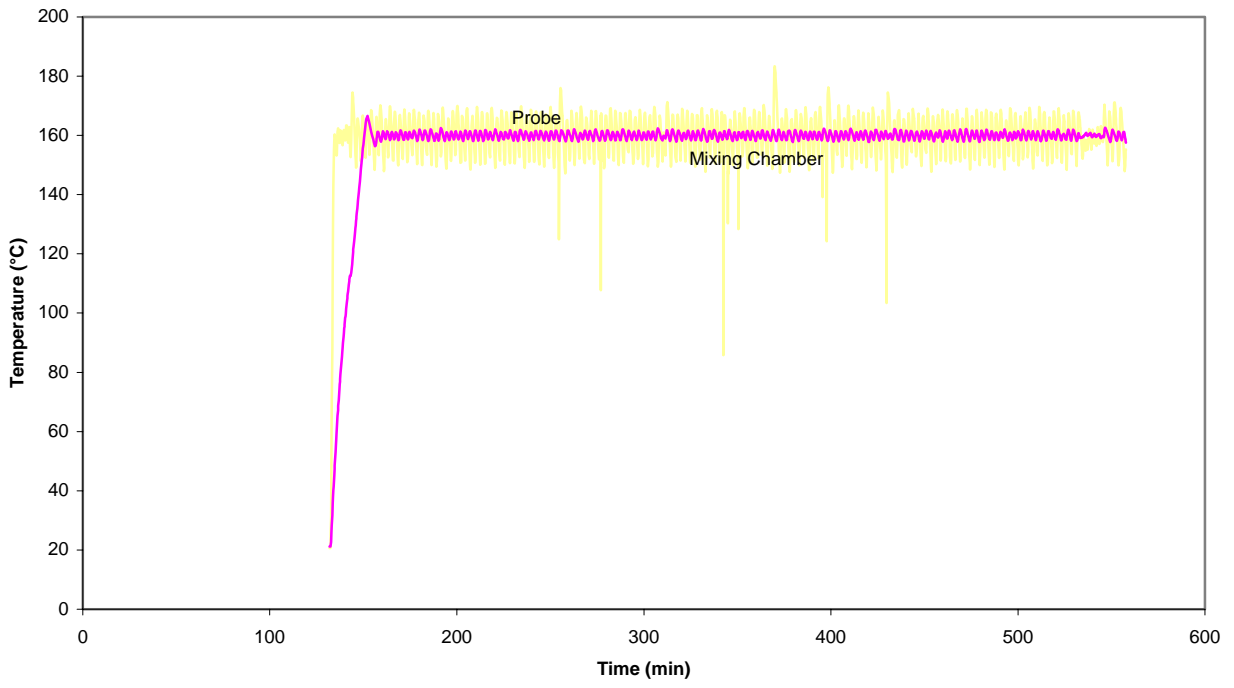


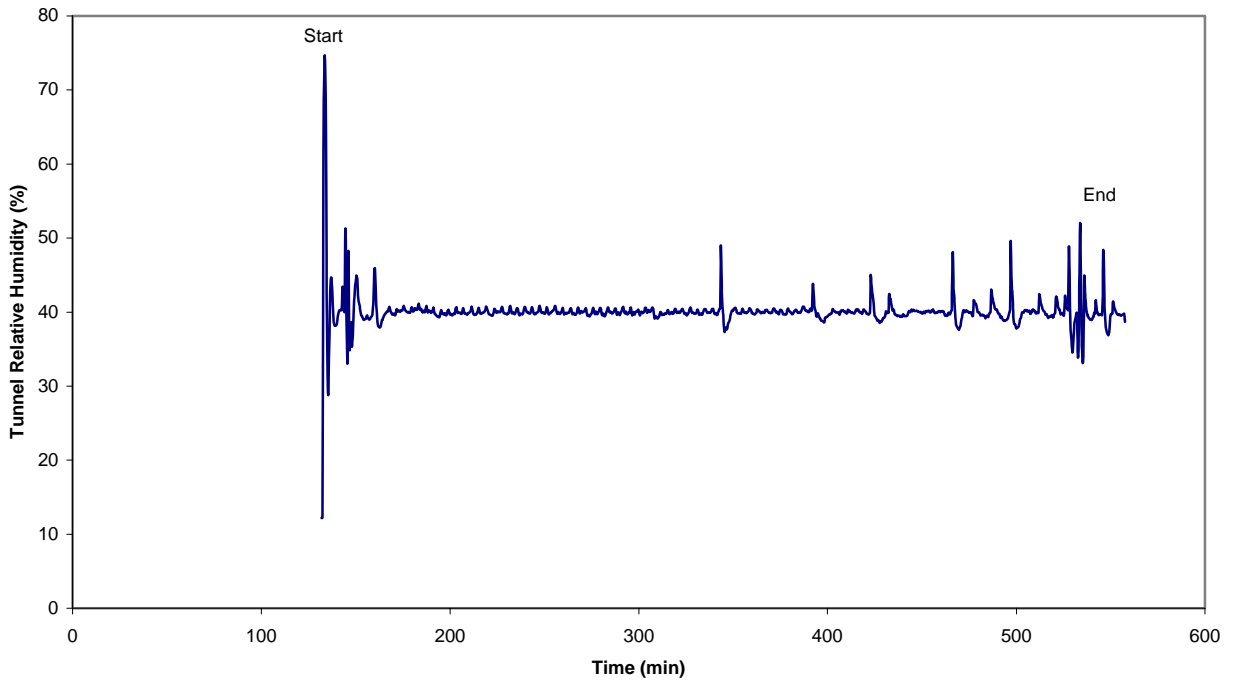
Figure 8 - Emission and temperature profiles from PM source dilution measurement experiment using LD-1000 test fuel

- (a) Carbon monoxide/dioxide, oxygen, nitrogen oxides and sulphur dioxide**
- (b) Stack, boiler, tunnel, and room temperature**
- (c) Mass flow of dilution air and sampling ports**
- (d) Control CO₂ concentration**
- (e) Probe and mixing chamber temperature**
- (f) Stack draft and draft over flame**
- (g) Tunnel relative humidity**









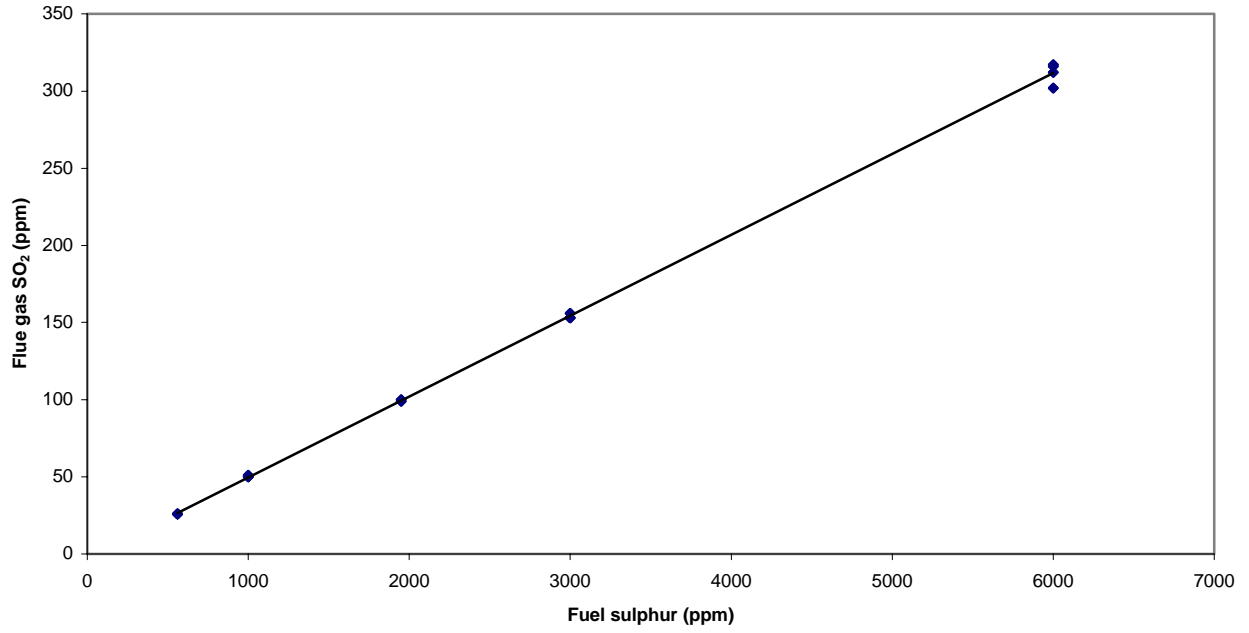


Figure 9 - Effect of fuel sulphur on flue gas SO₂ emissions

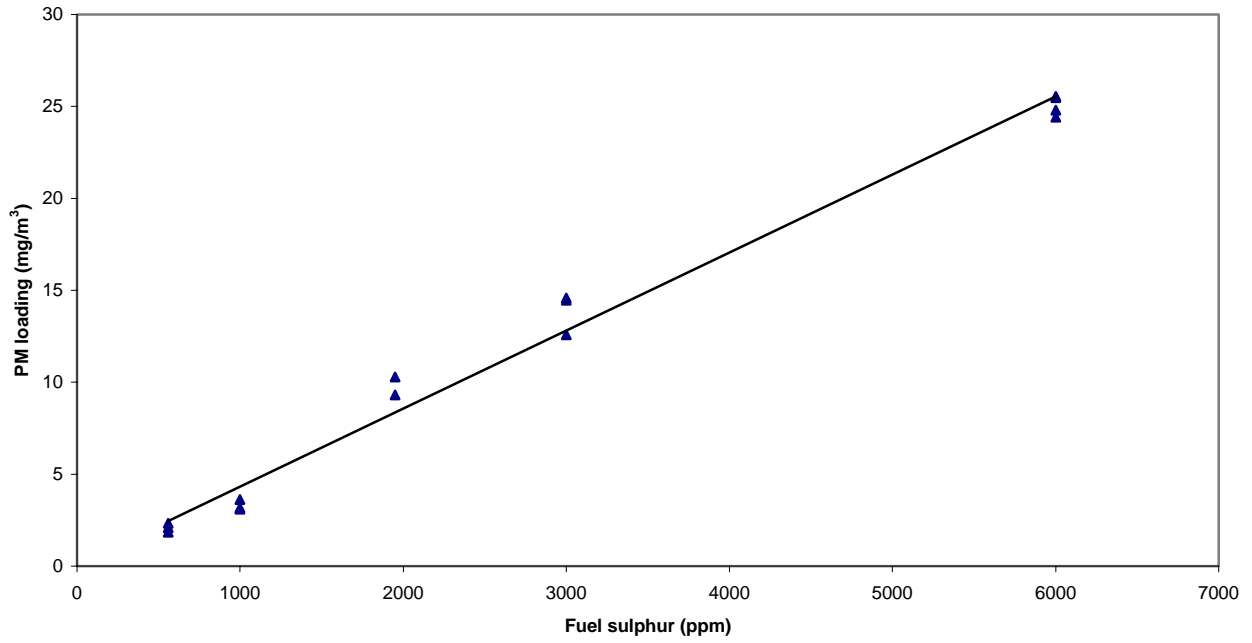


Figure 10 - Effect of fuel sulphur on total PM emissions

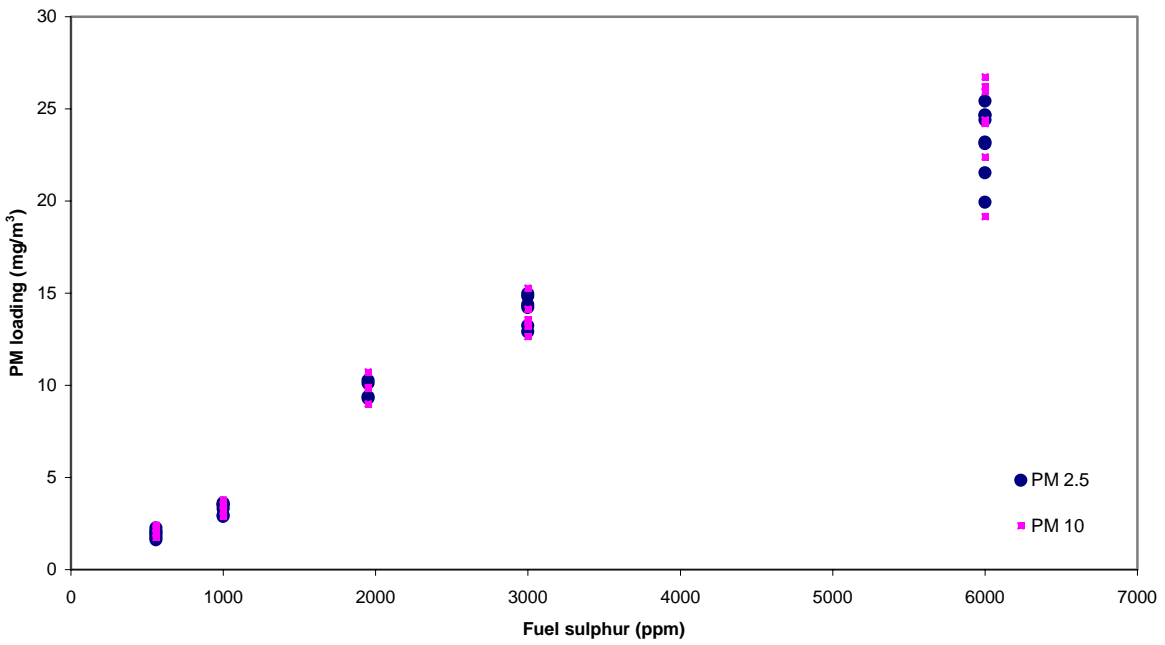


Figure 11 - Effect of fuel sulphur on PM_{2.5} and PM₁₀ emissions

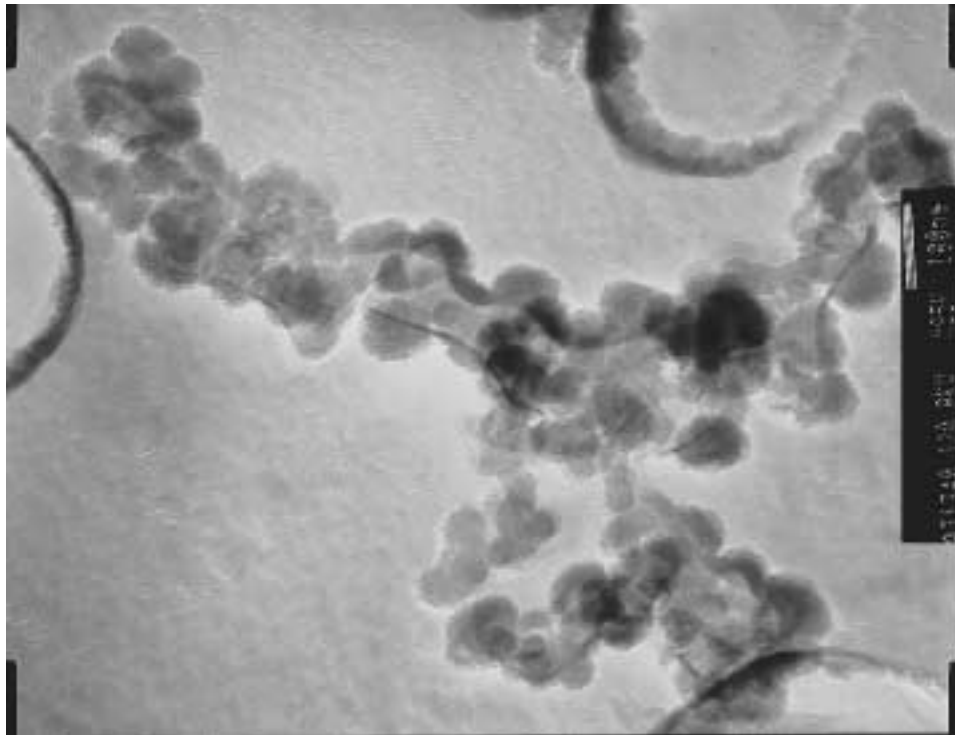


Figure 12 - Typical transmission electron micrograph of PM_{2.5} agglomerate for LD-500 fuel at 85,000 magnification

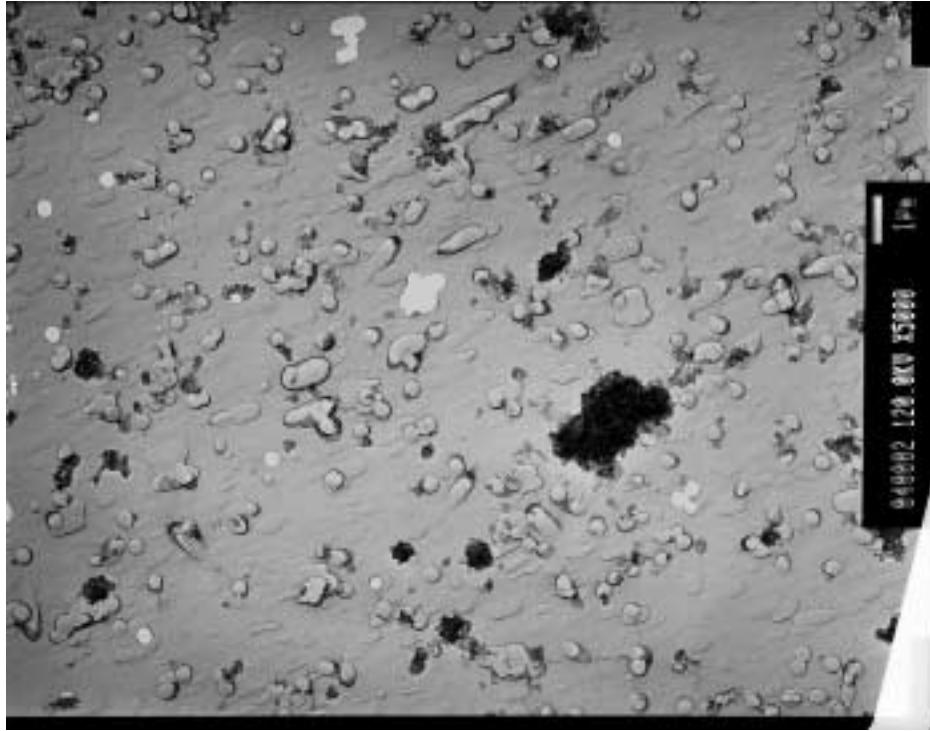


Figure 13 - Typical field image from TEM of PM_{2.5} for LD-500 fuel at 5000 magnification

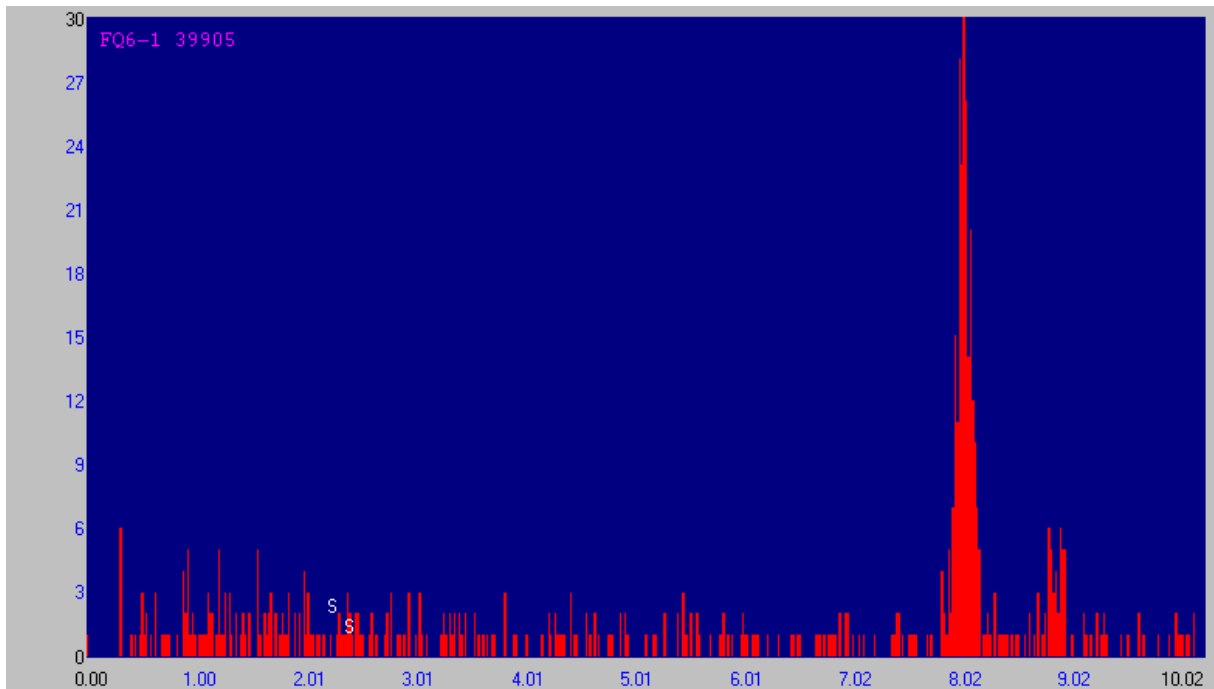


Figure 14 - Typical elemental spectrum of PM_{2.5} agglomerate for LD-500 fuel

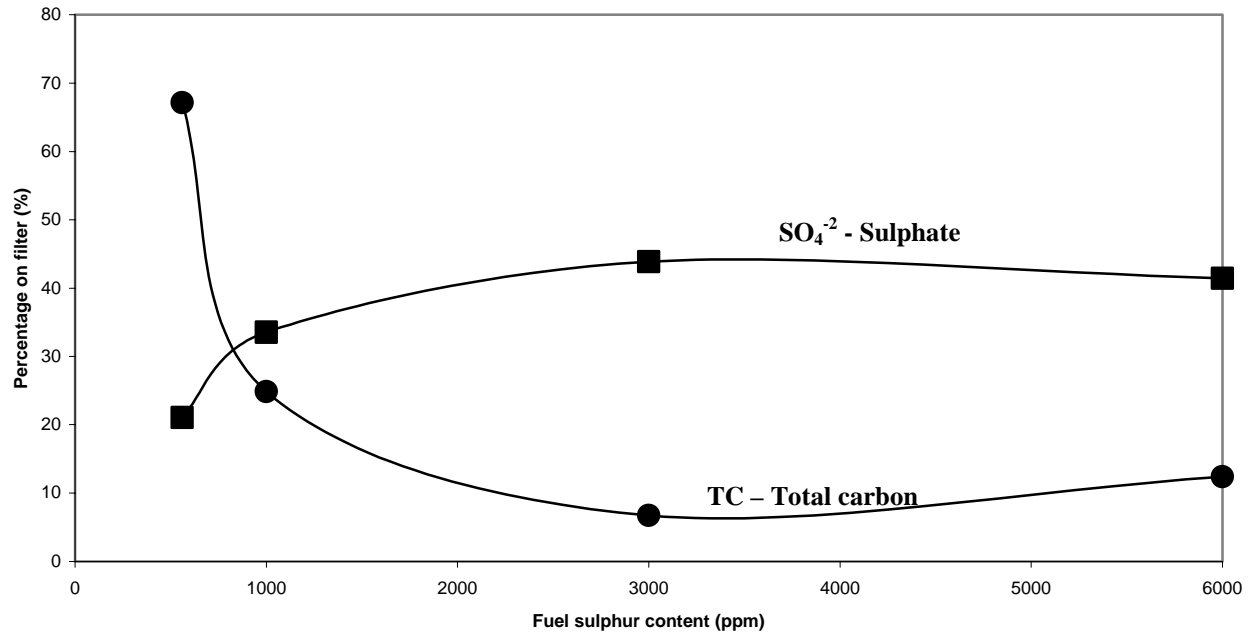


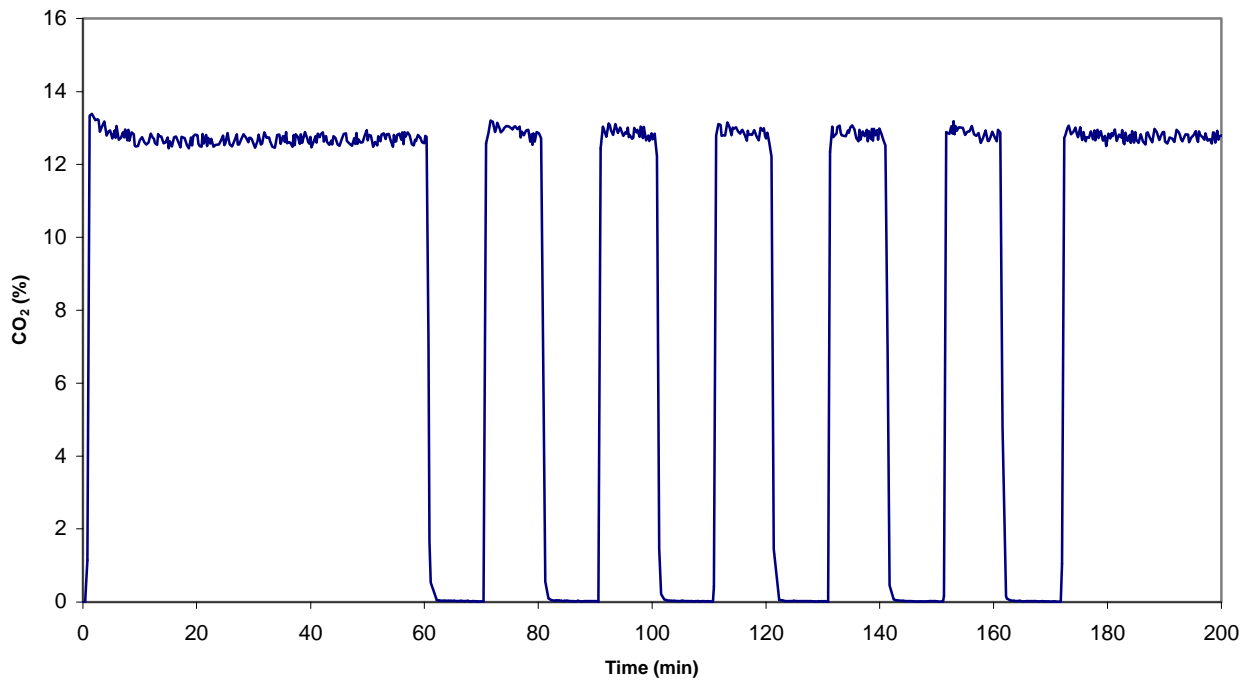
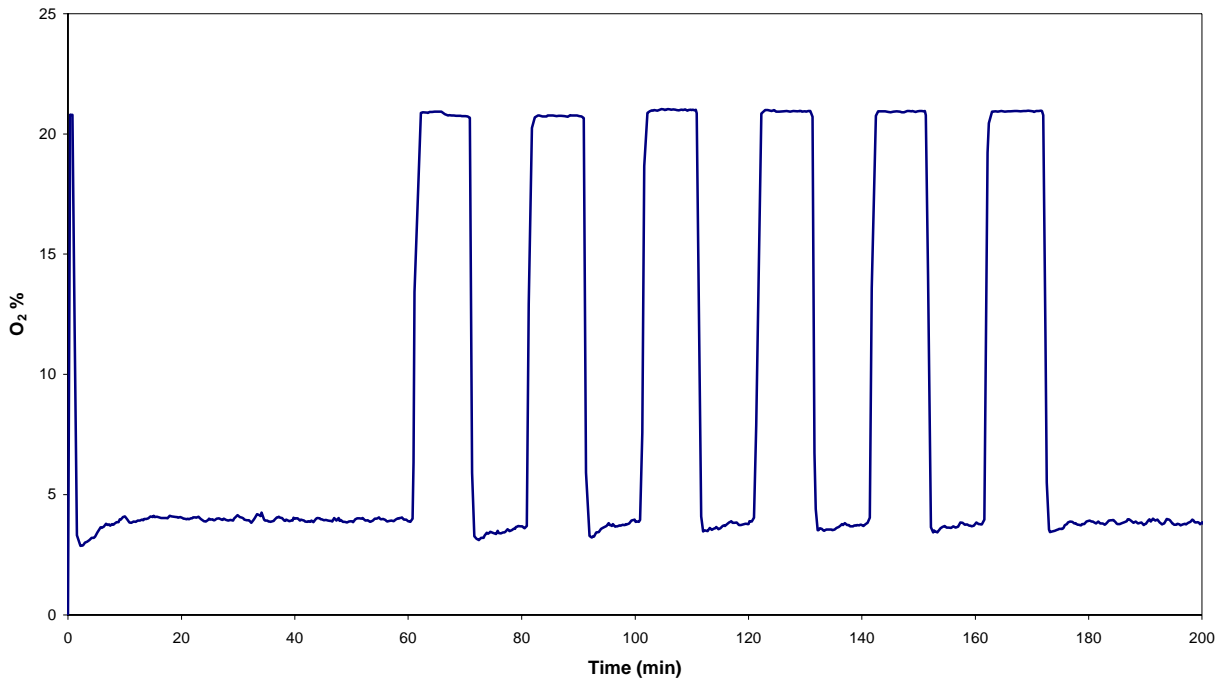
Figure 15 - Effect of fuel sulphur on sulphate and total carbon contents of PM

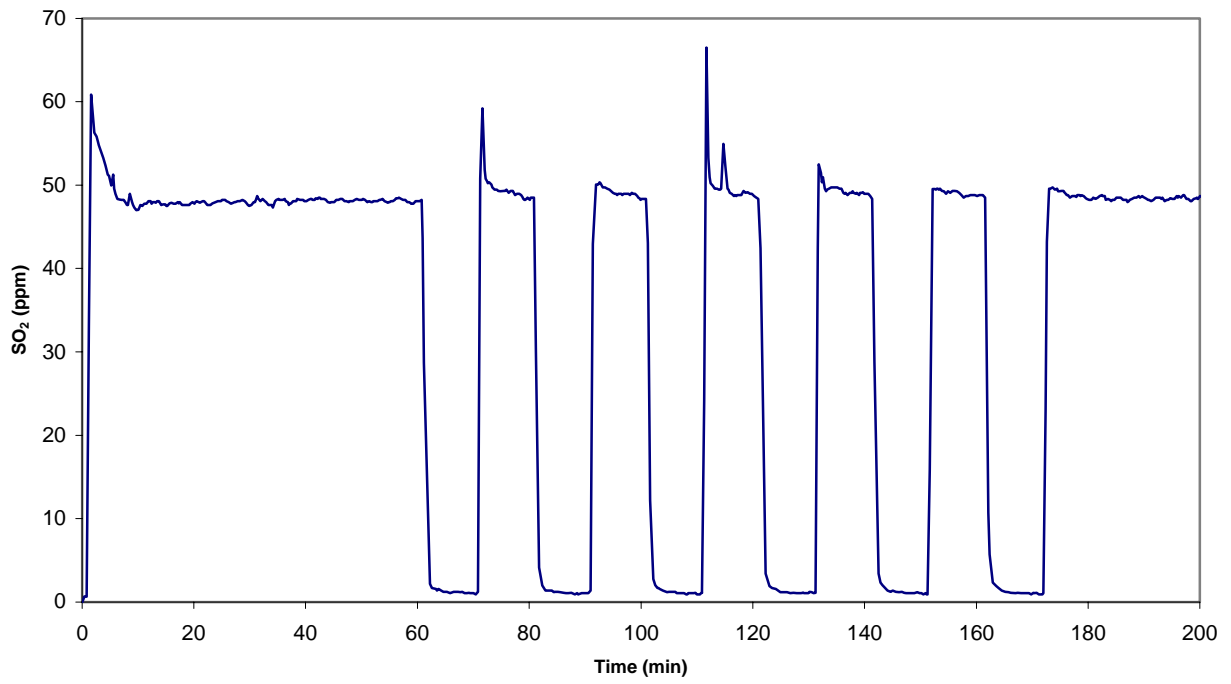
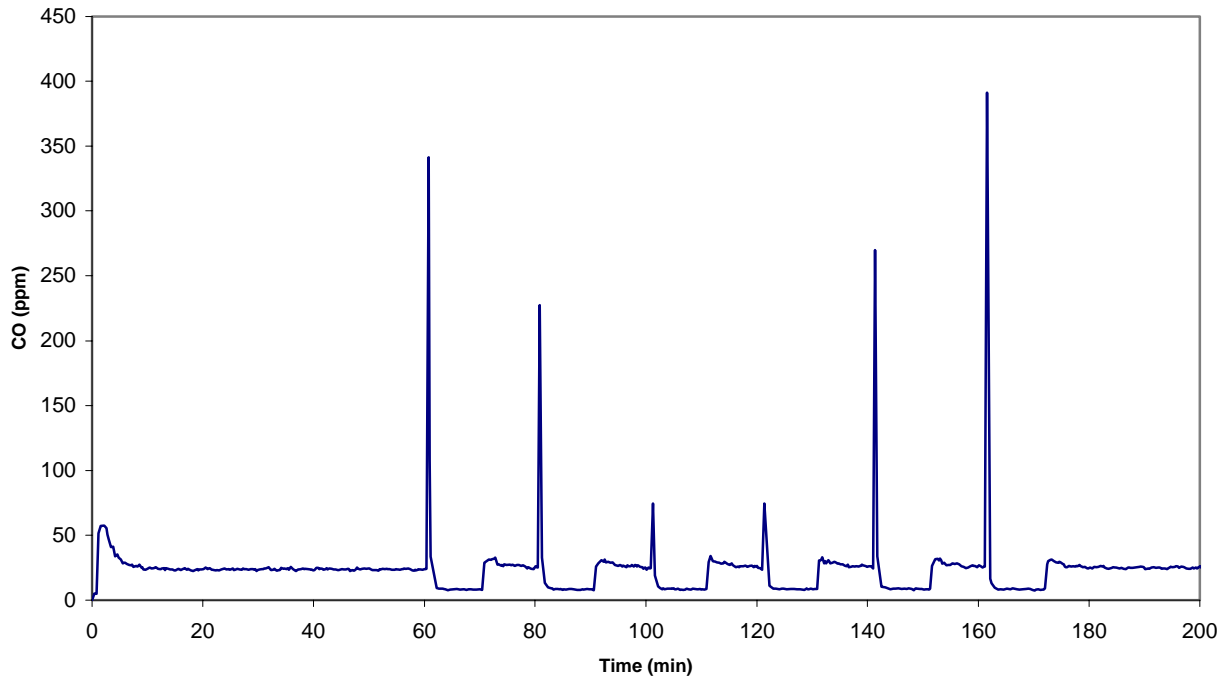
APPENDIX A

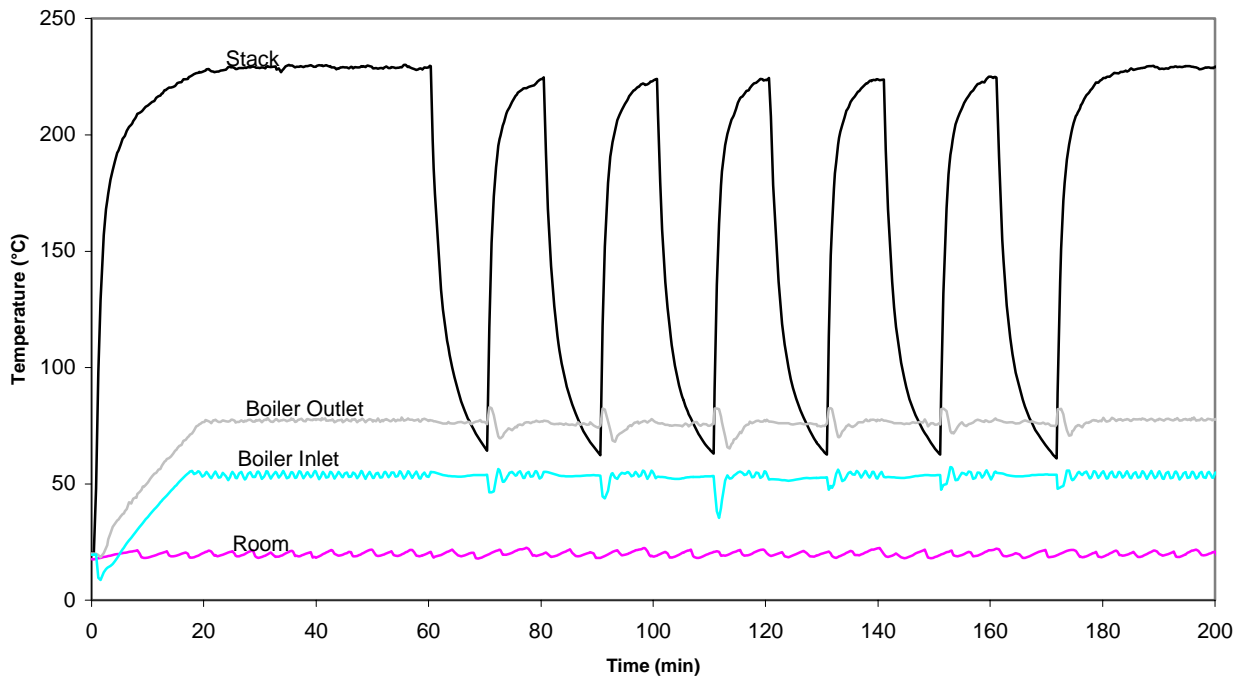
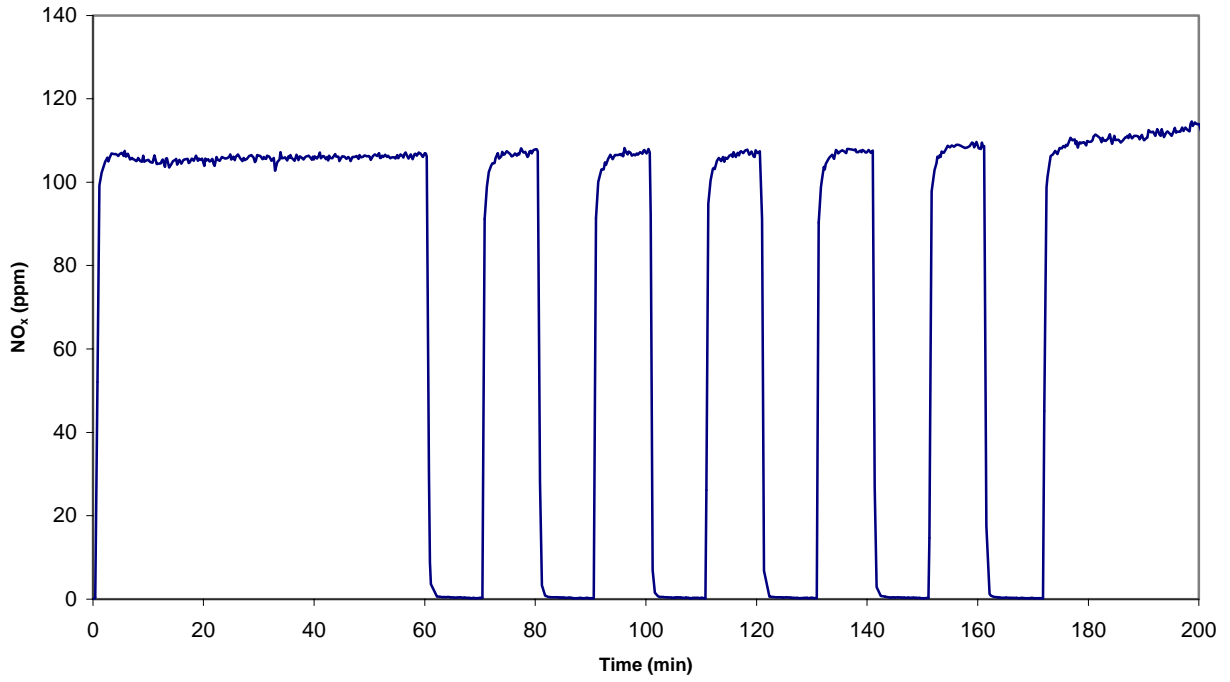
Temperature and emission profiles

Figure A1 - Emission and temperature profiles from a combustion experiment using LD-1000 fuel

- (a) Oxygen concentration**
- (b) Carbon dioxide concentration**
- (c) Carbon monoxide concentration**
- (d) Sulphur dioxide concentration**
- (e) Nitrogen oxide concentration**
- (f) Stack, boiler and room temperature profiles**
- (g) Stack draft and draft over flame**







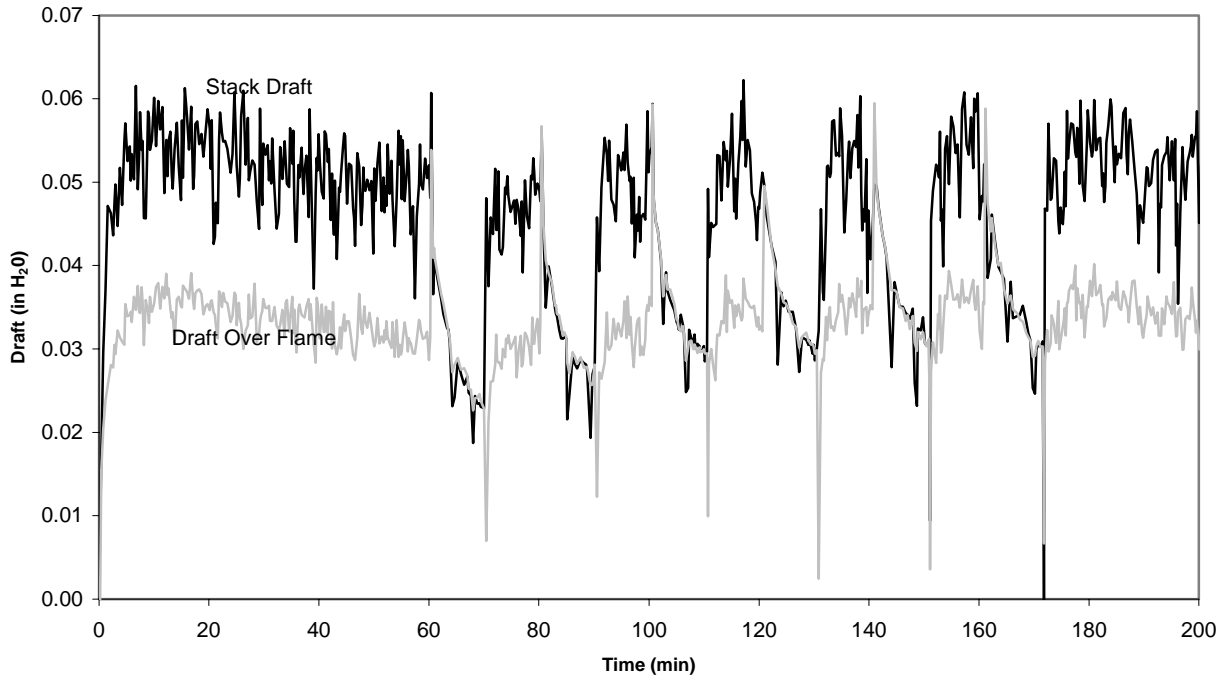
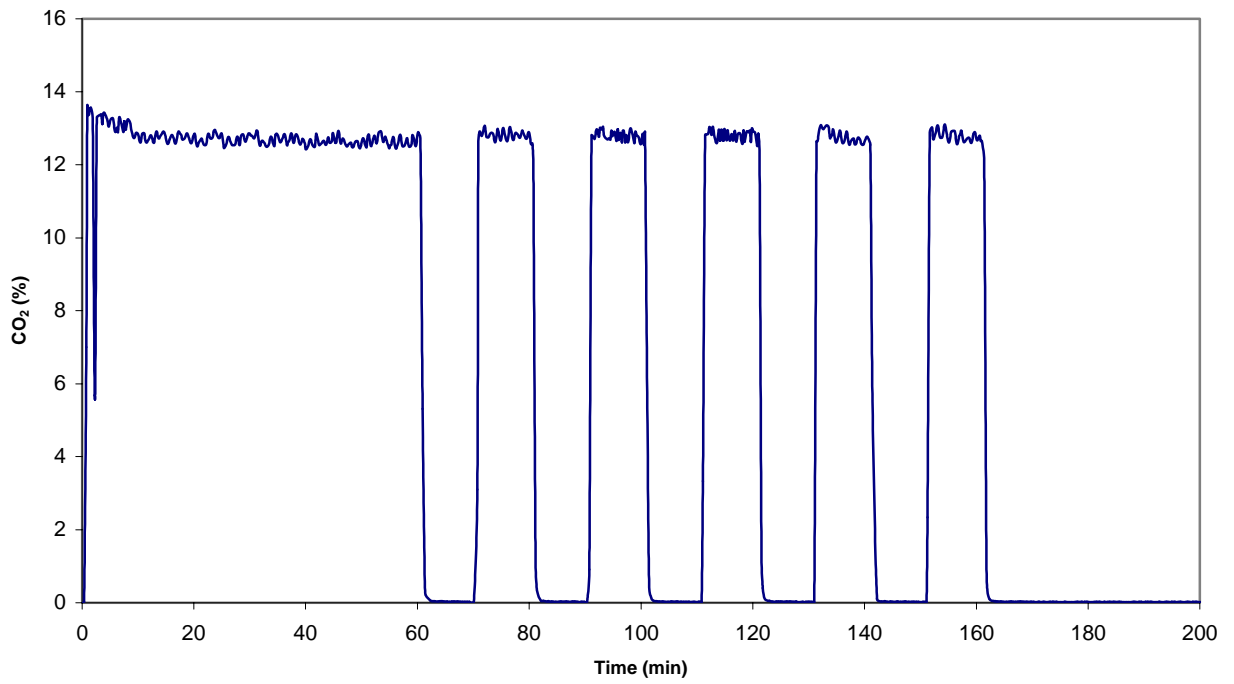
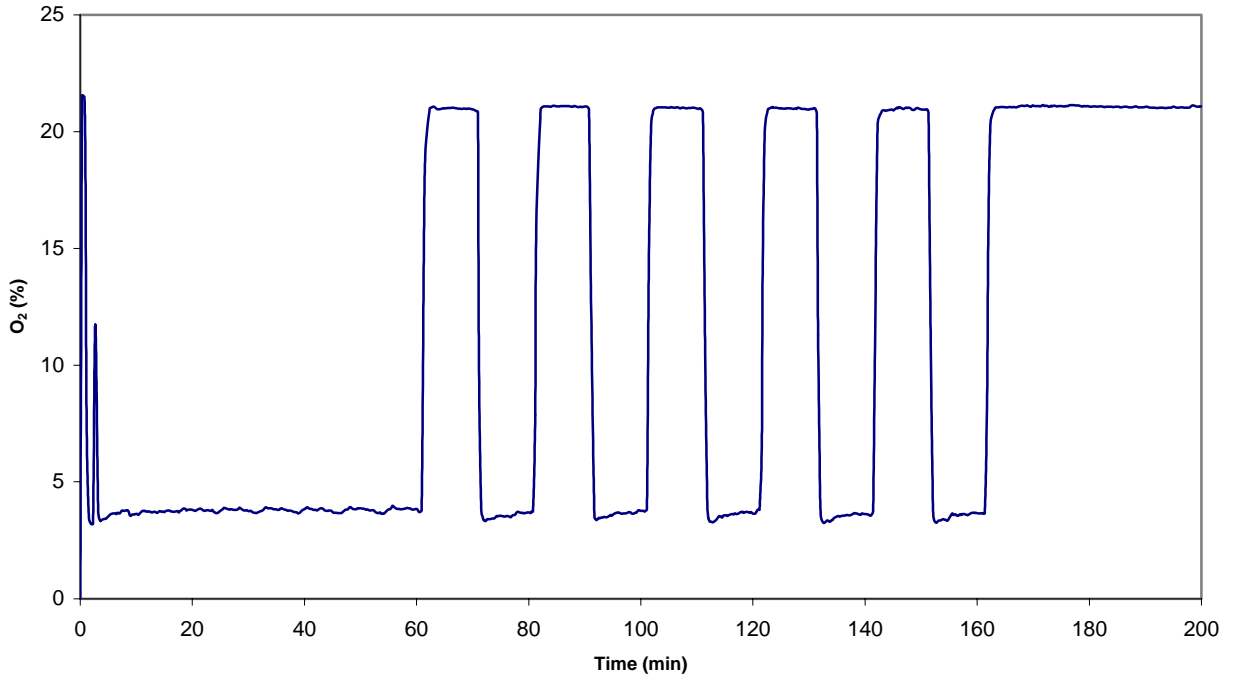
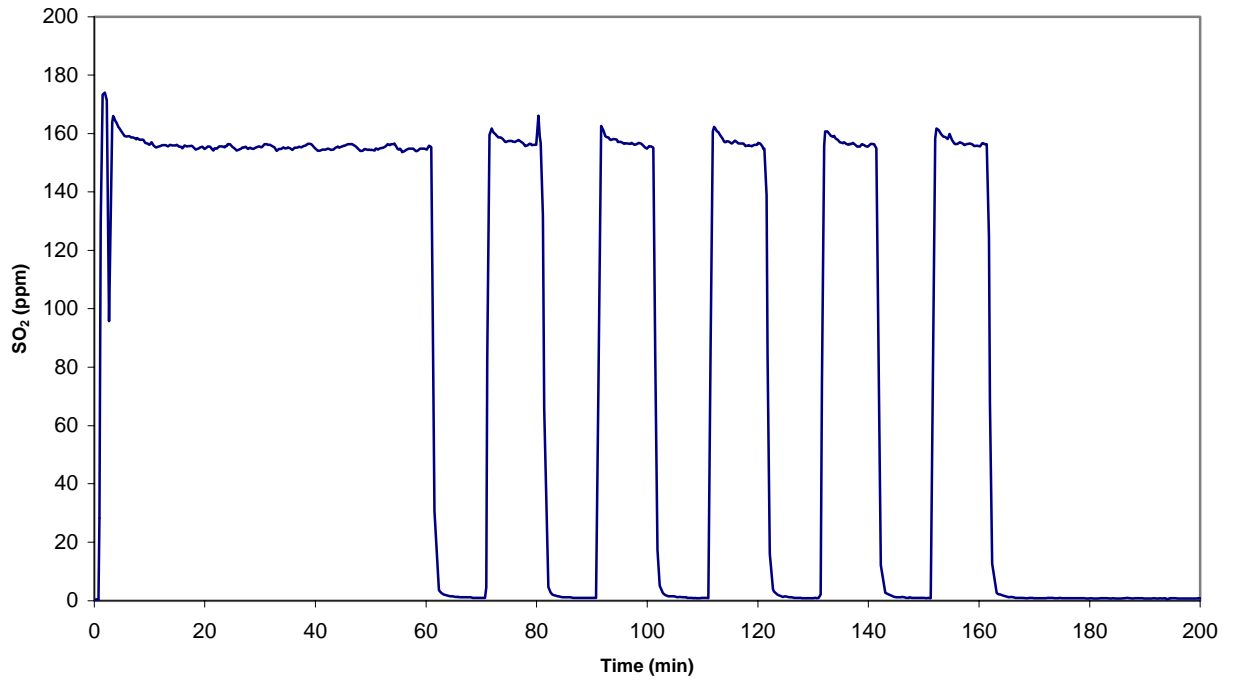
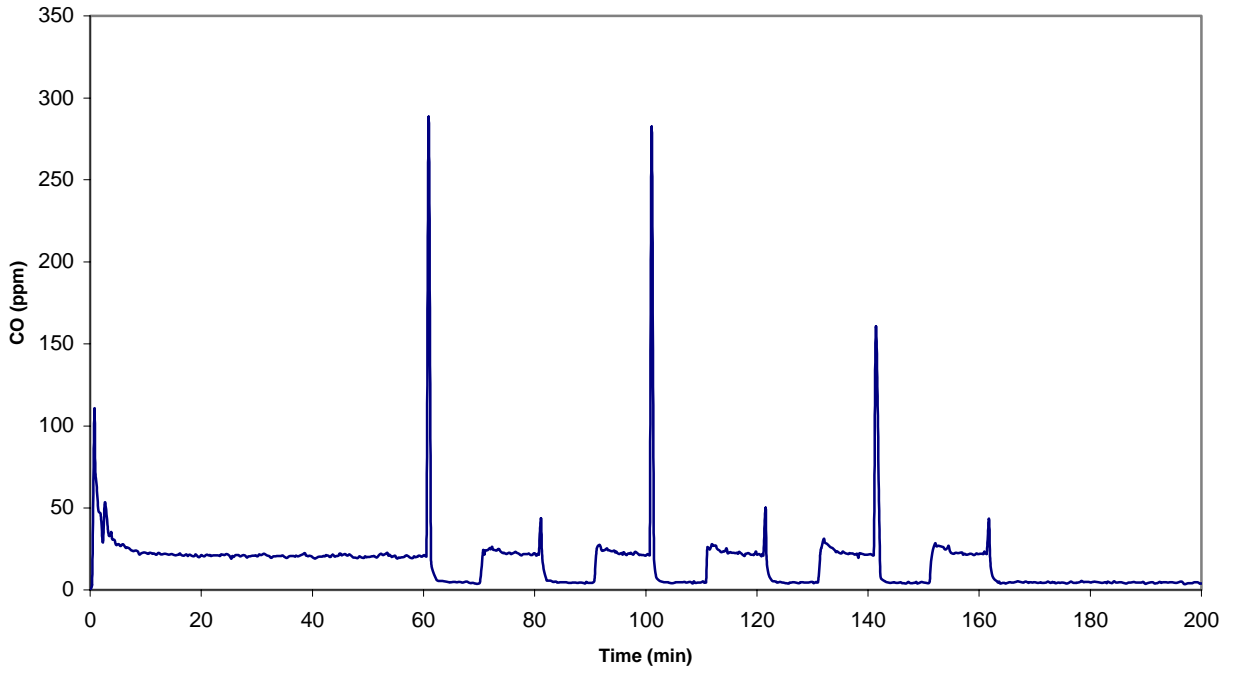
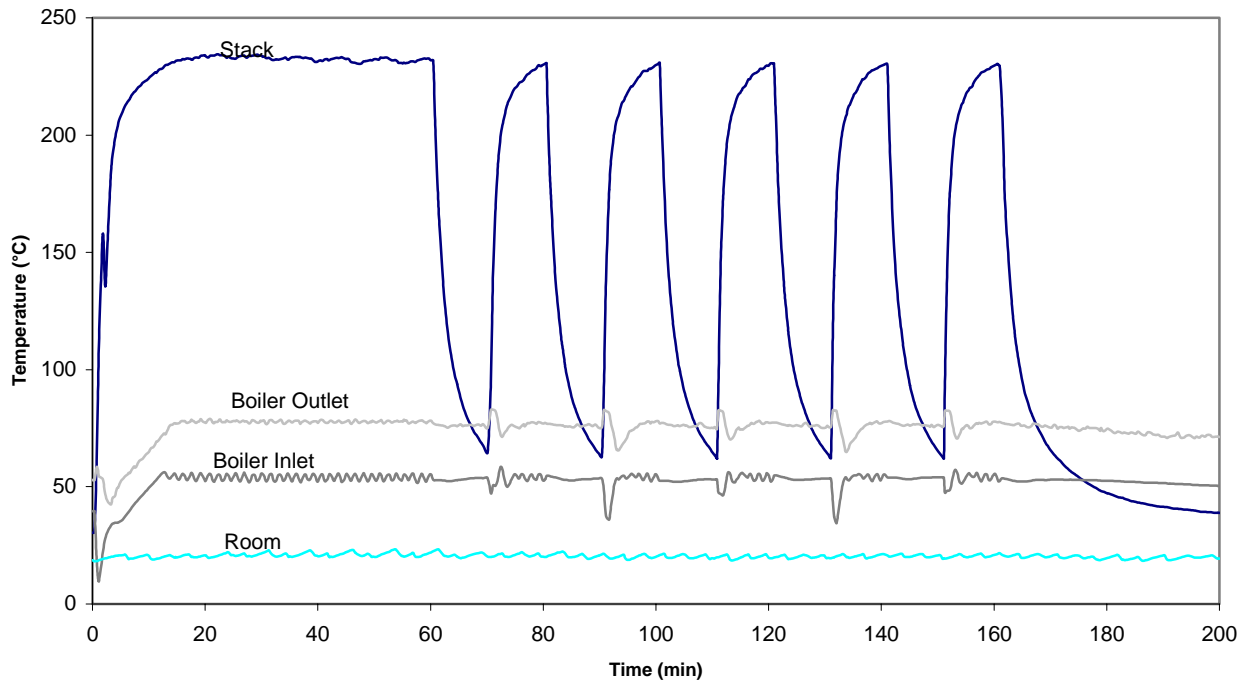
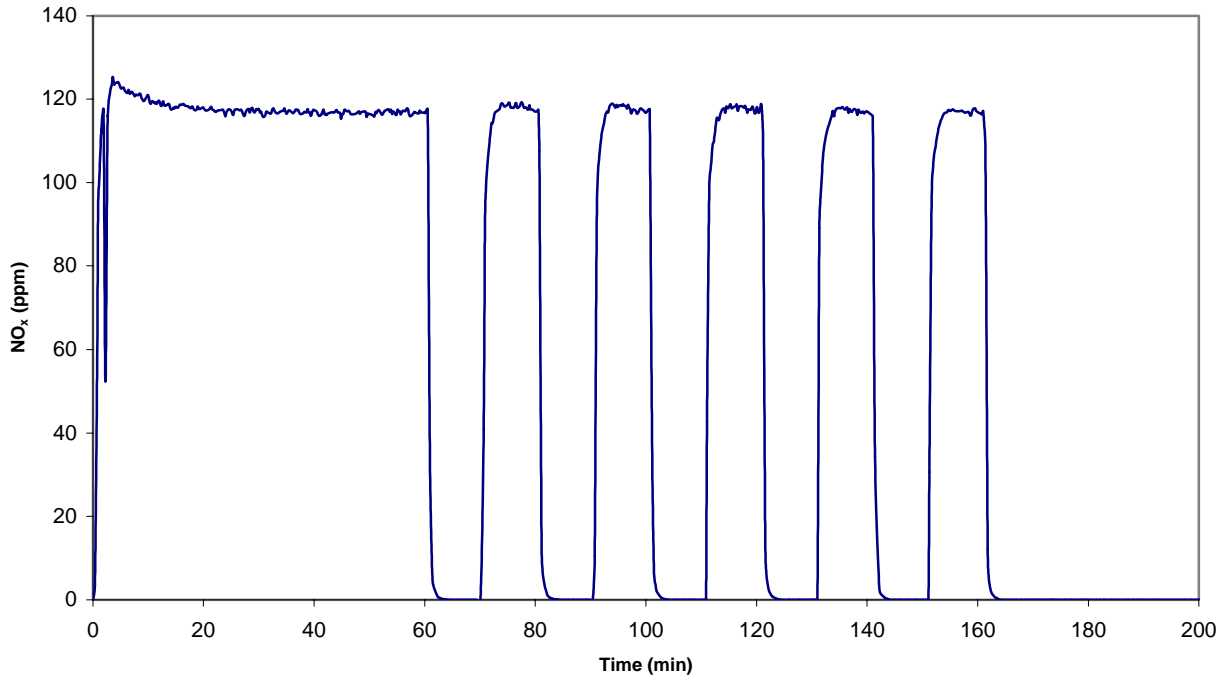


Figure A2 - Emission and temperature profiles from a combustion experiment using LD-3000 fuel

- (a) Oxygen concentration**
- (b) Carbon dioxide concentration**
- (c) Carbon monoxide concentration**
- (d) Sulphur dioxide concentration**
- (e) Nitrogen oxide concentration**
- (f) Stack, boiler and room temperature profiles**
- (g) Stack draft and draft over flame**







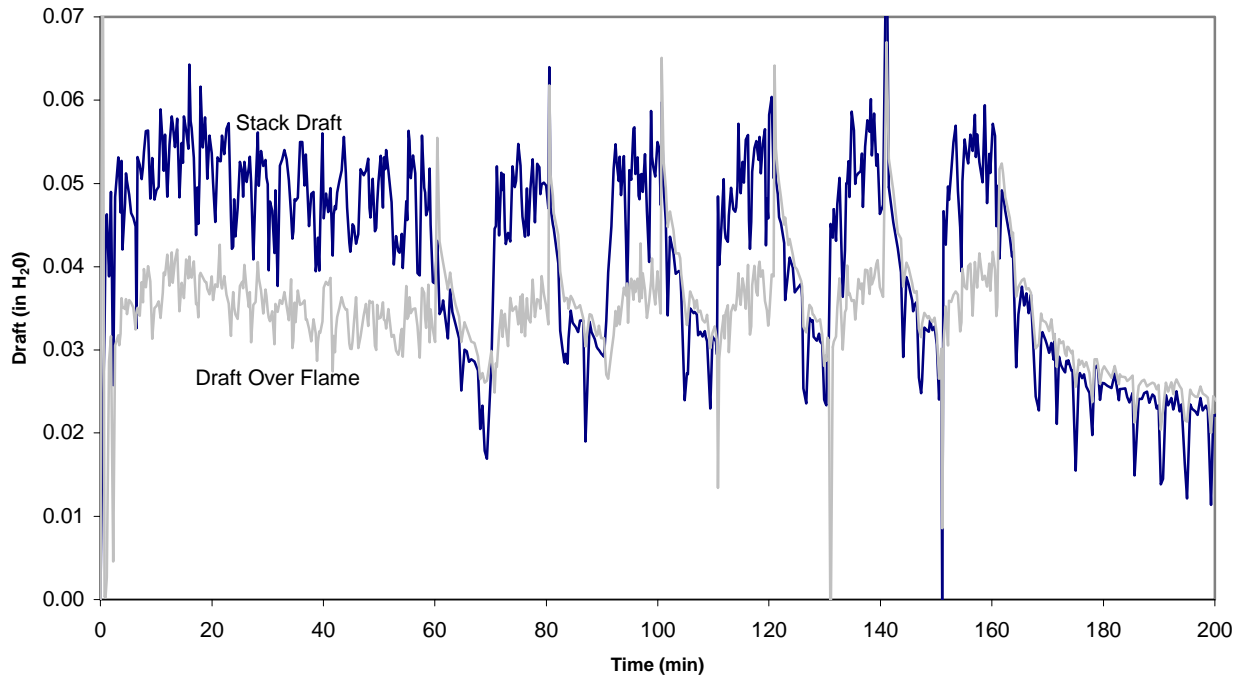
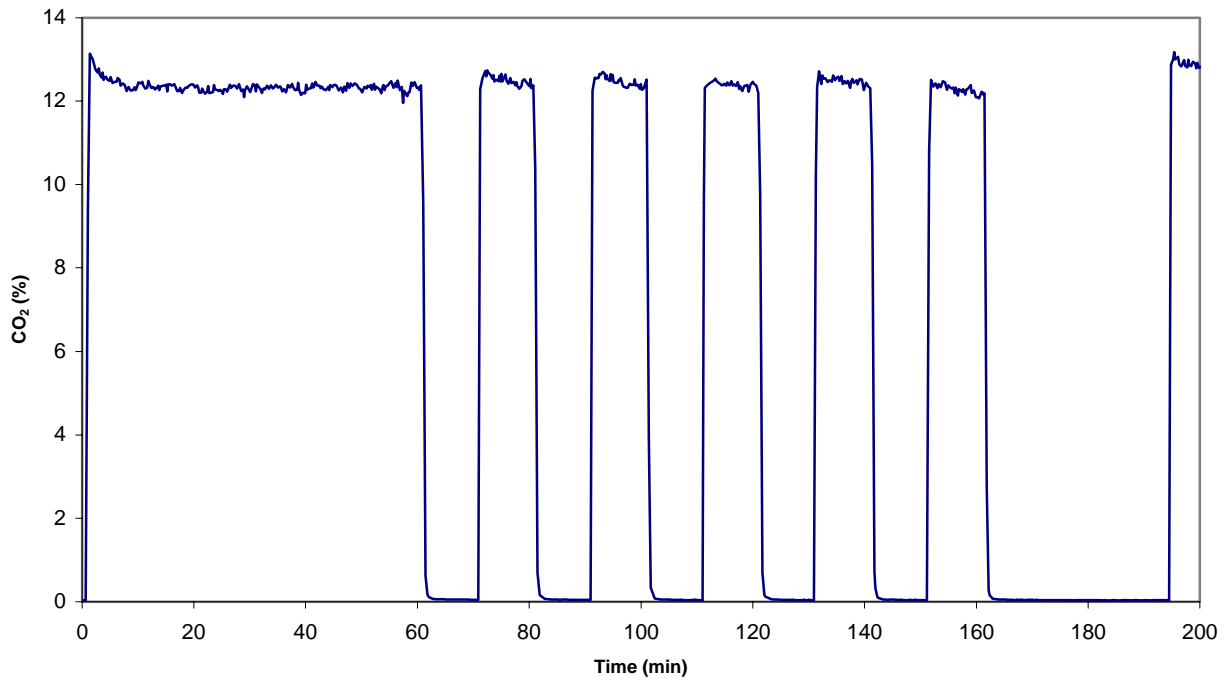
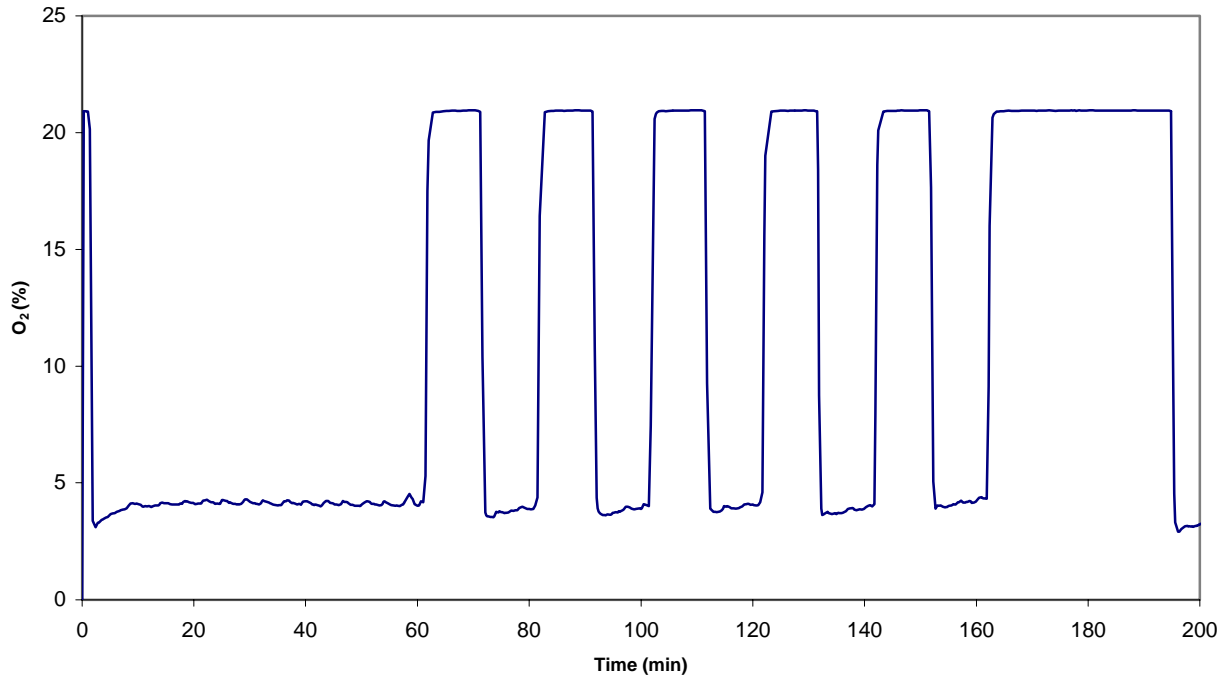
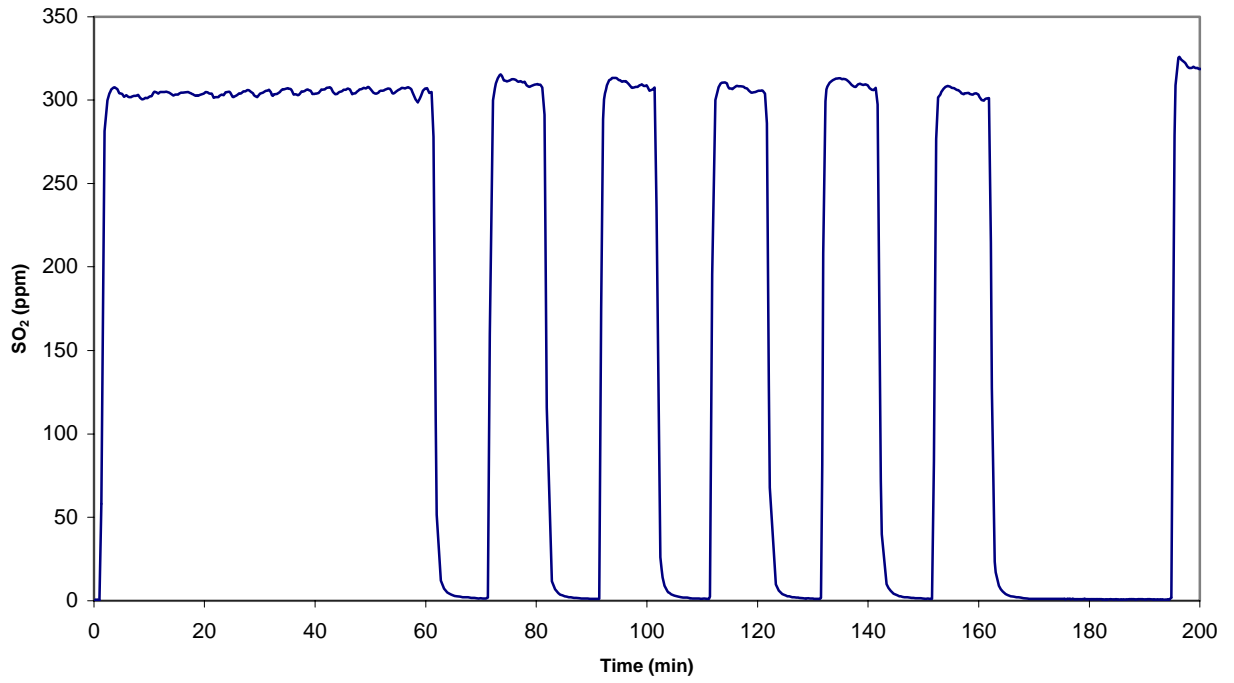
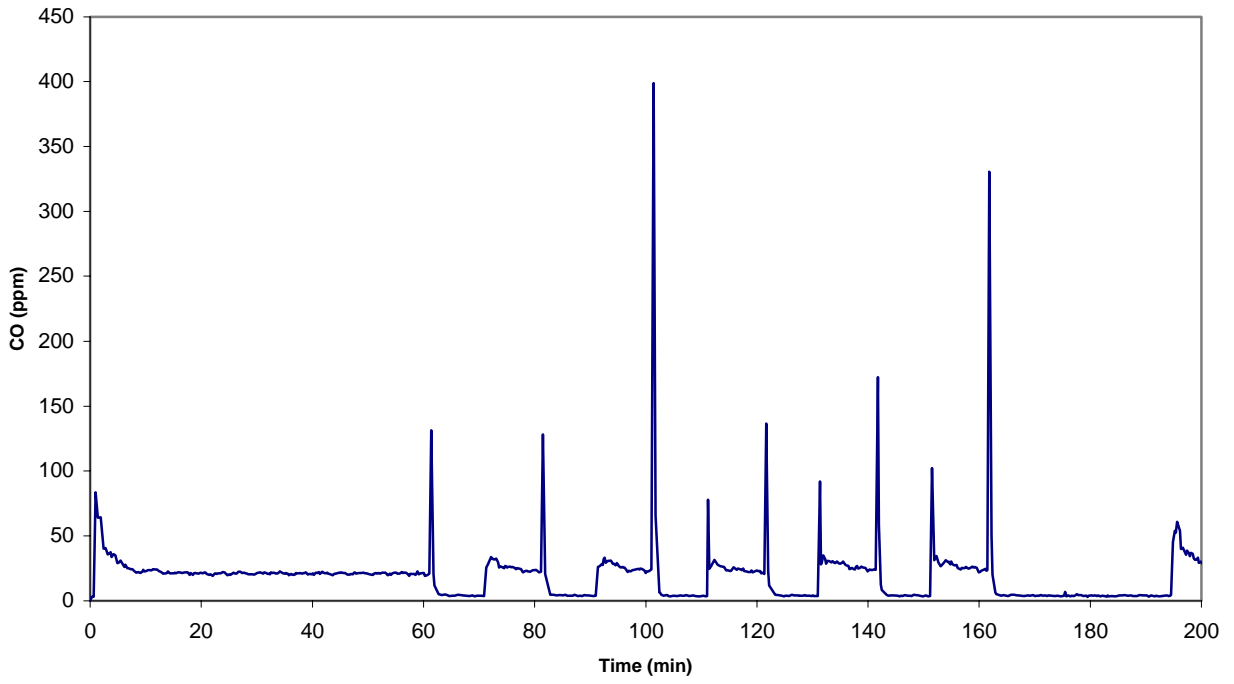
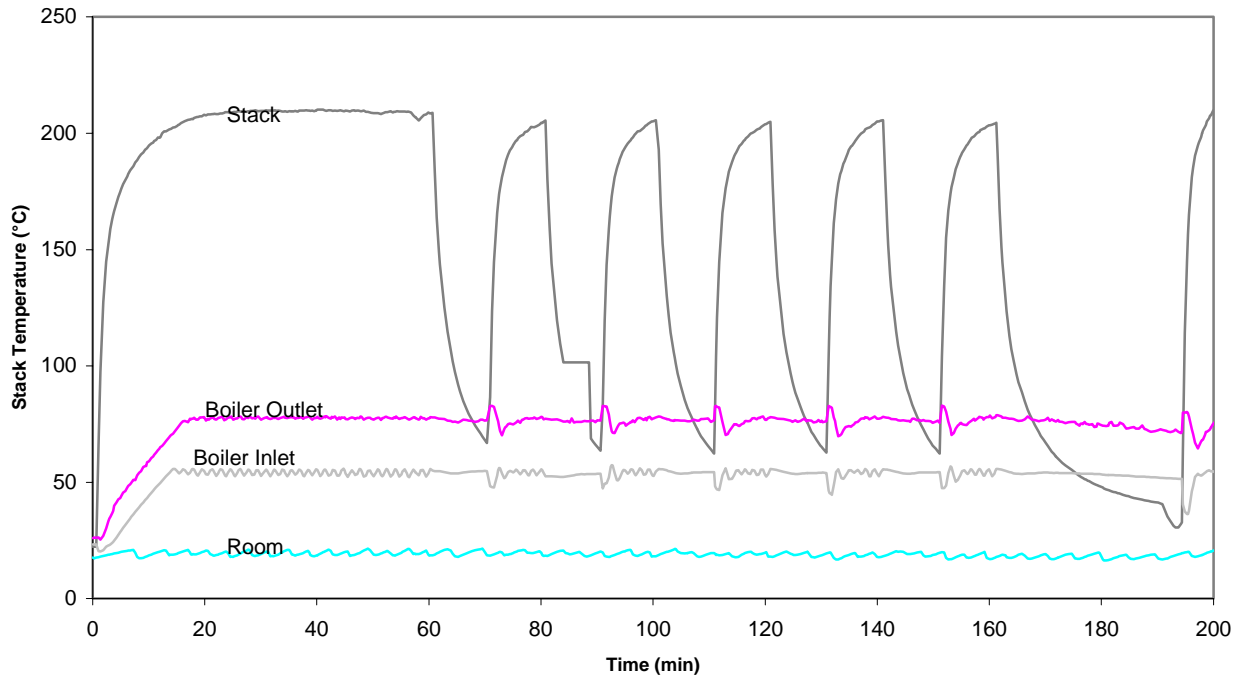
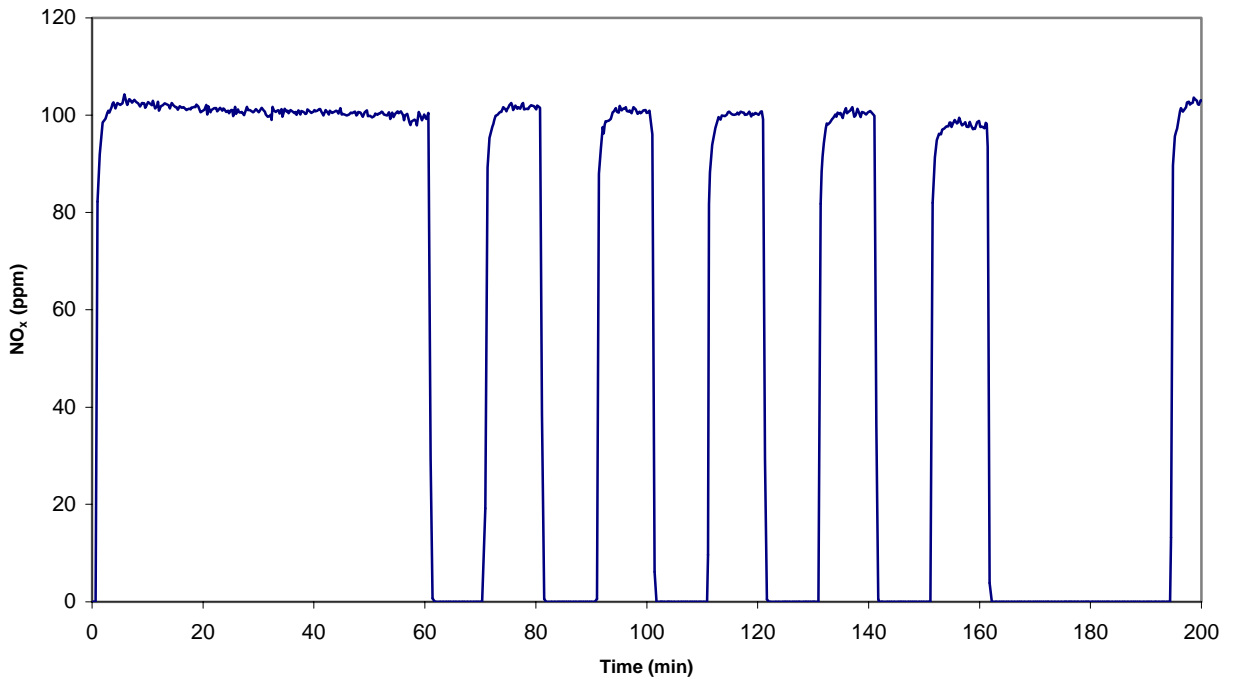


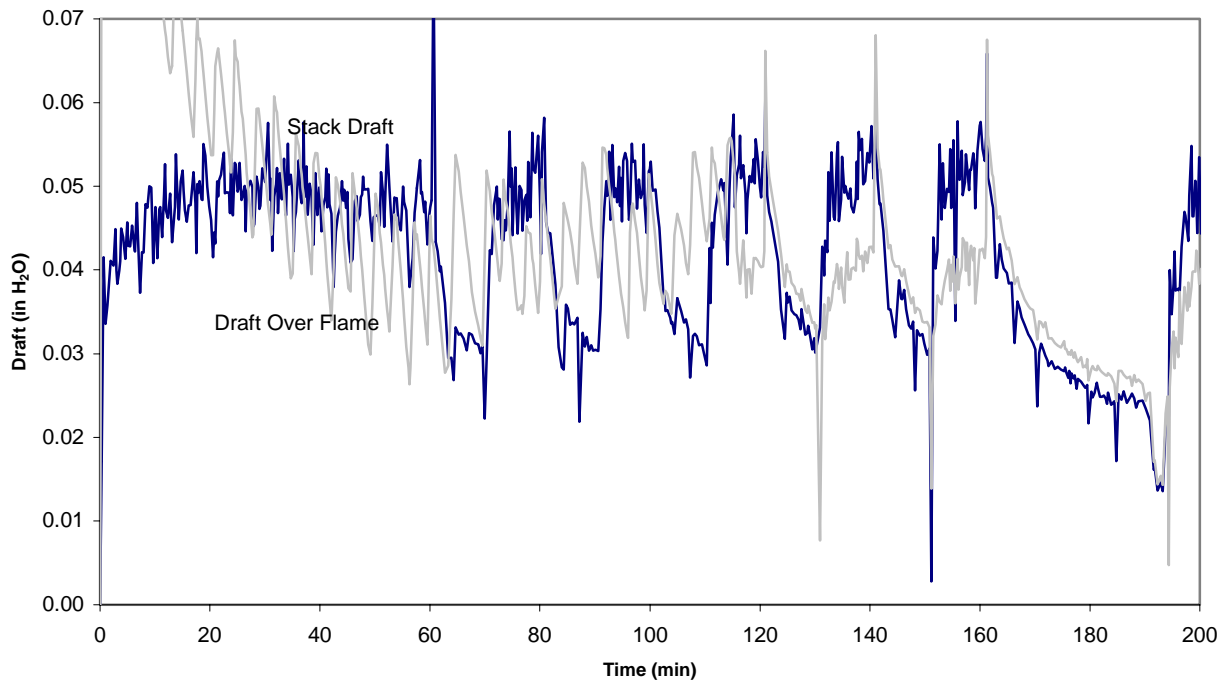
Figure A3 - Emission and temperature profiles from a combustion experiment using LD-6000 fuel

- (a) Oxygen concentration**
- (b) Carbon dioxide concentration**
- (c) Carbon monoxide concentration**
- (d) Sulphur dioxide concentration**
- (e) Nitrogen oxide concentration**
- (f) Stack, boiler and room temperature profiles**
- (g) Stack draft and draft over flame**









APPENDIX B

TEM Images

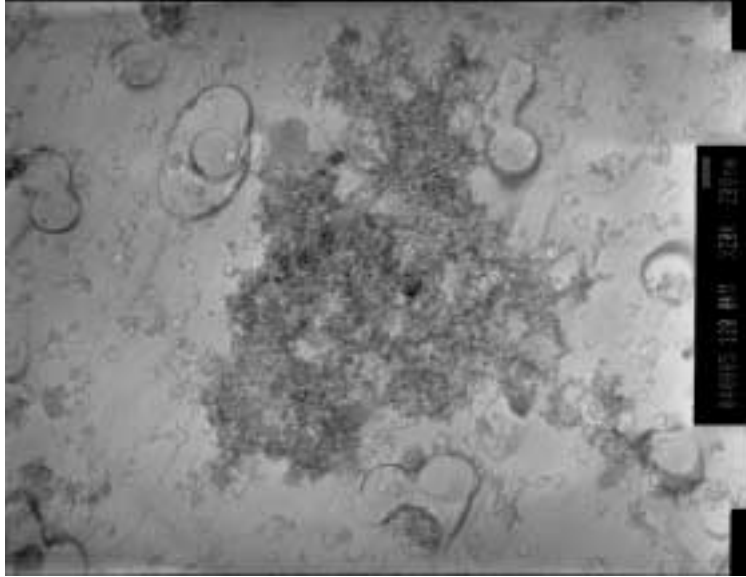


Figure B1 - Typical transmission electron micrograph of PM₁₀ agglomerate for LD-500 fuel at 100,000 magnification

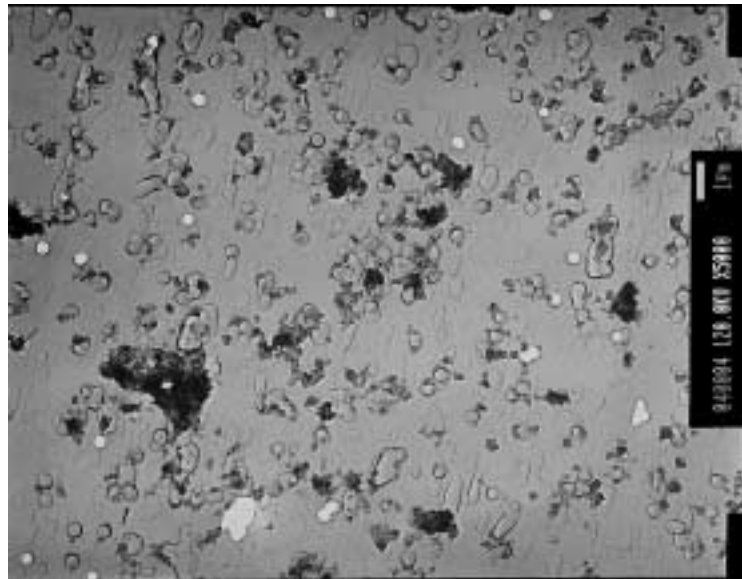


Figure B2 - Typical image from TEM of PM₁₀ for LD-500 fuel at 5000 magnification

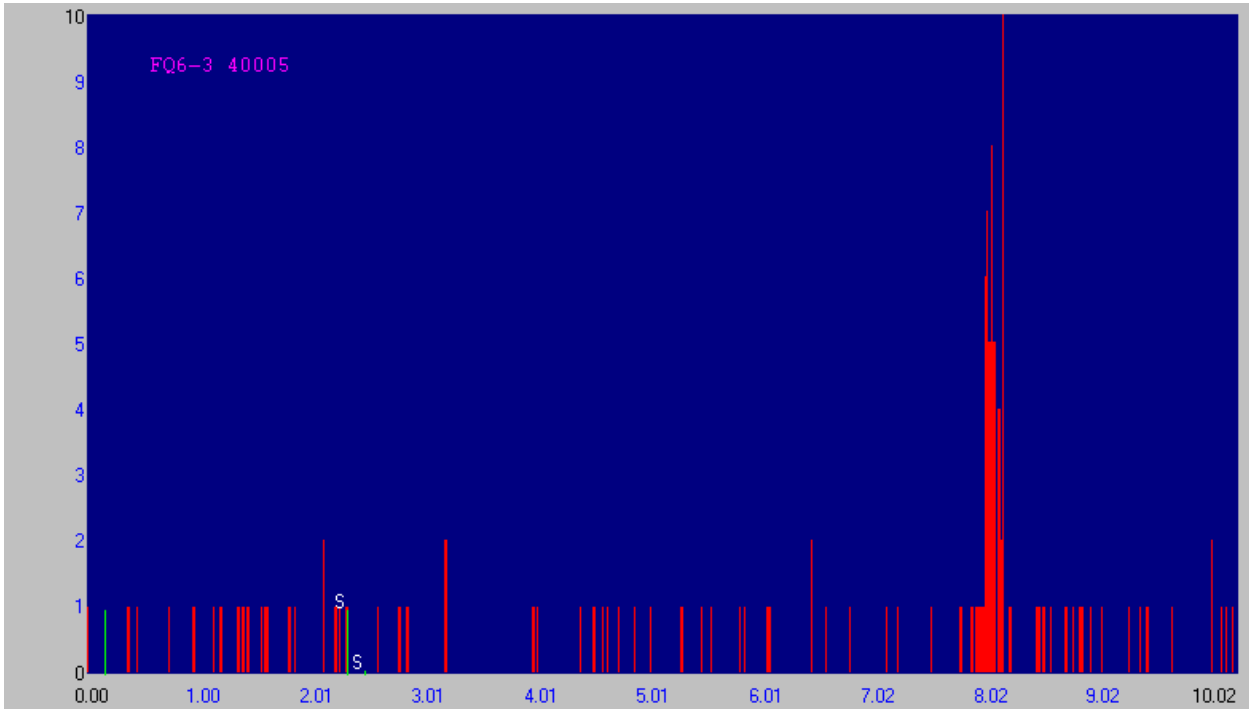


Figure B3 - Typical elemental spectrum of PM₁₀ agglomerate for LD-500 fuel

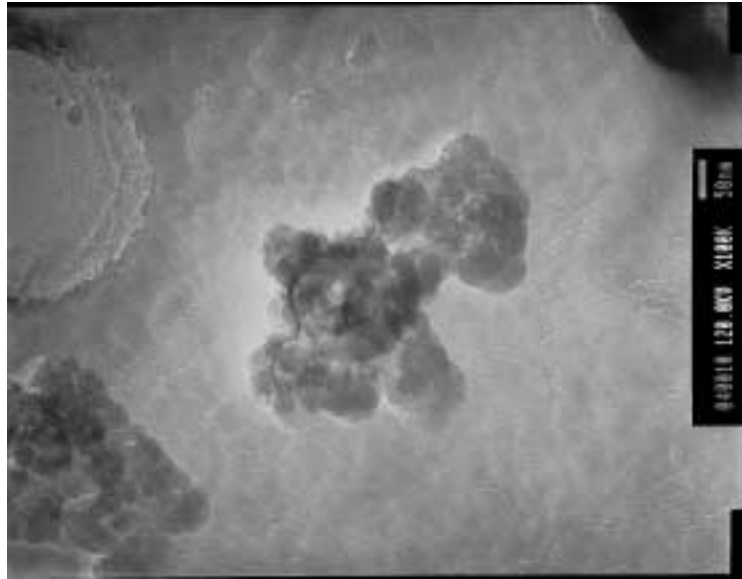


Figure B4 - Typical transmission electron micrograph of PM_{Total} agglomerate for LD-500 fuel at 100,000 magnification

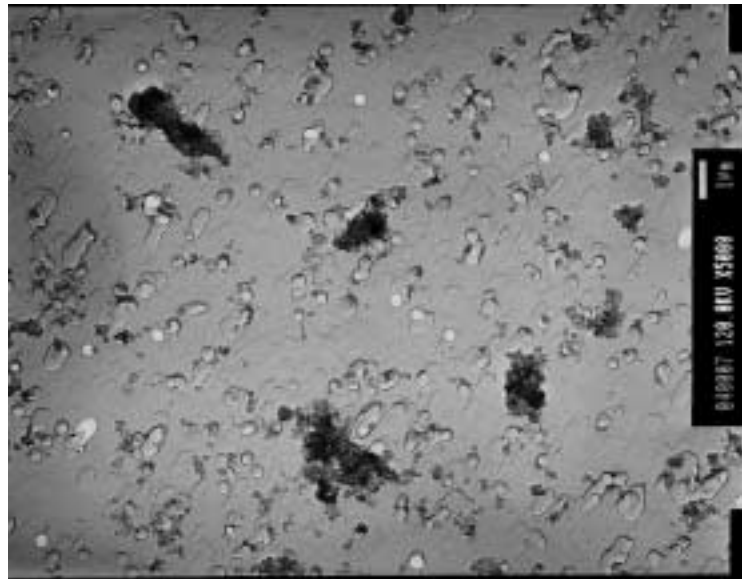


Figure B5 - Typical image from TEM of PM_{Total} for LD-500 fuel at 5000 magnification

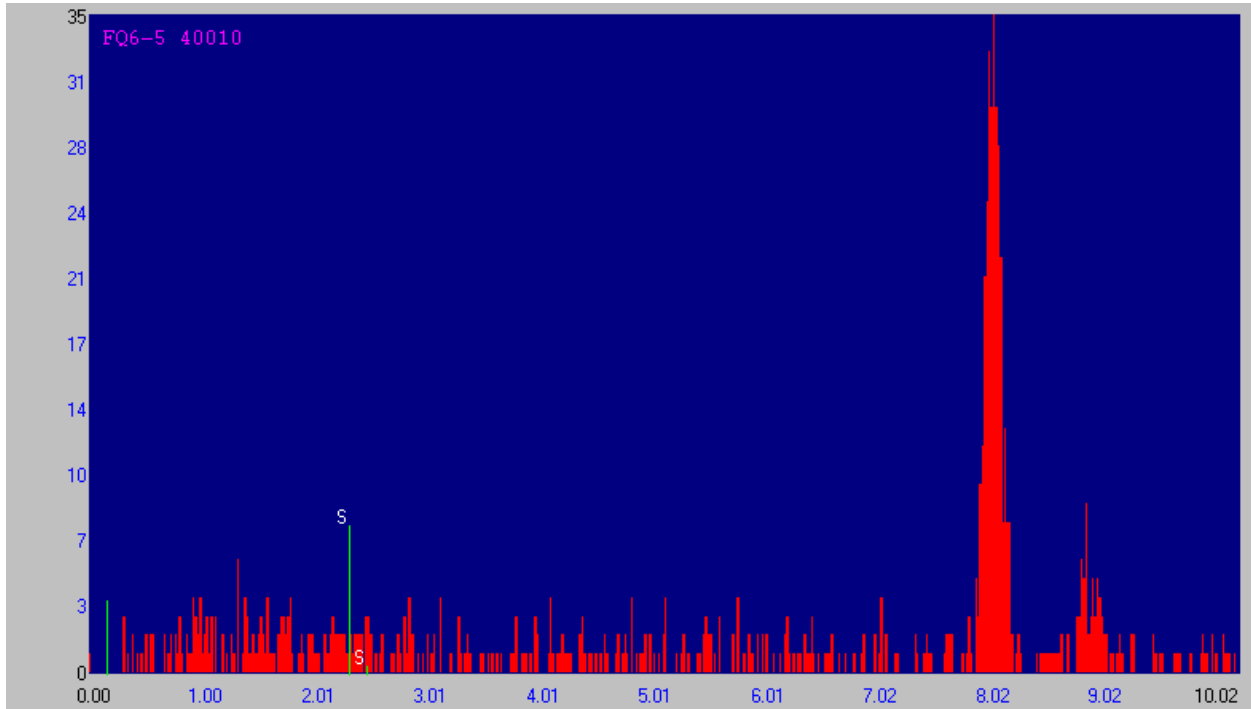


Figure B6 - Typical elemental spectrum of PM_{Total} agglomerate for LD-500 fuel

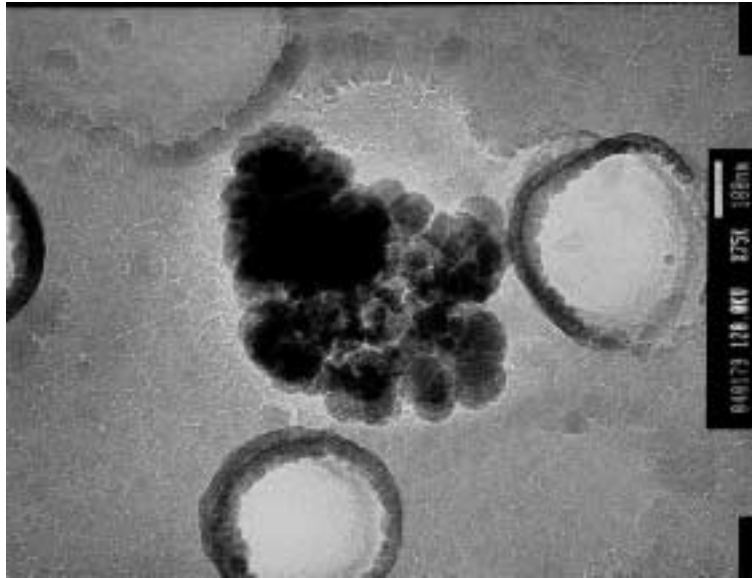


Figure B7 - Typical transmission electron micrograph of PM₁₀ agglomerate for No. 2 fuel at 75,000 magnification

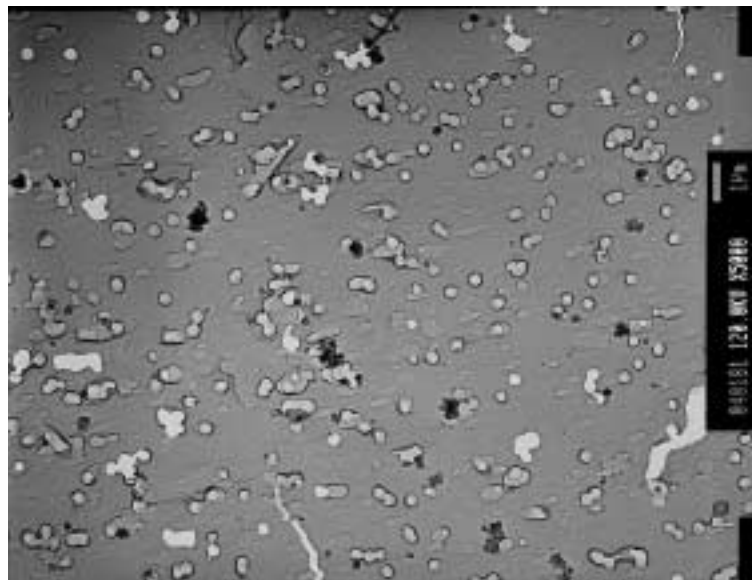


Figure B8 - Typical image from TEM of PM₁₀ for No. 2 fuel at 5000 magnification

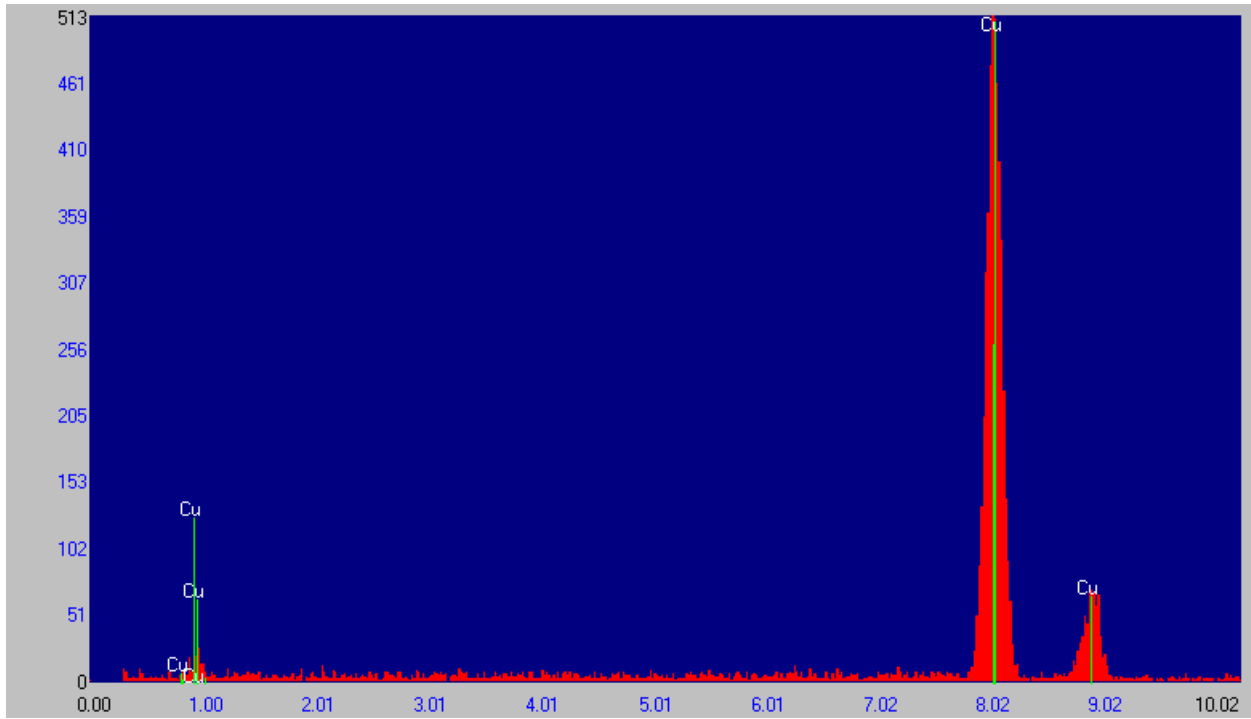


Figure B9 - Typical elemental spectrum of PM₁₀ agglomerate for No. 2 fuel

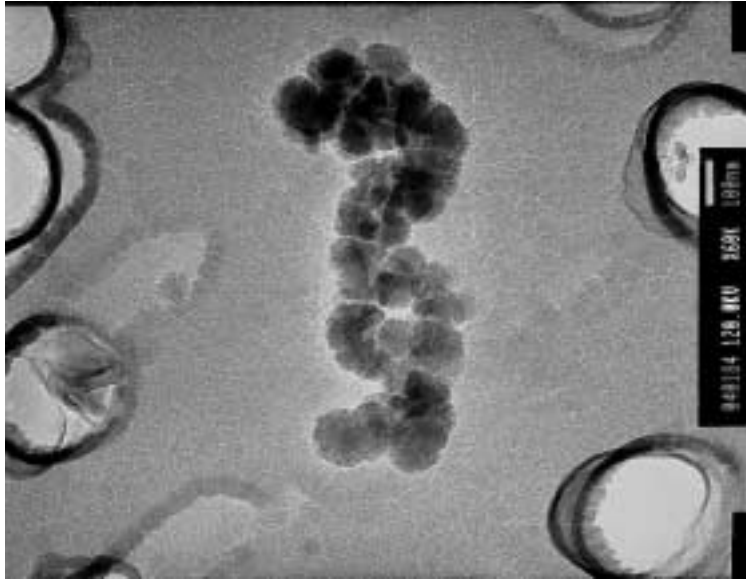


Figure B10 - Typical transmission electron micrograph of PM_{Total} agglomerate for No. 2 fuel at 60,000 magnification

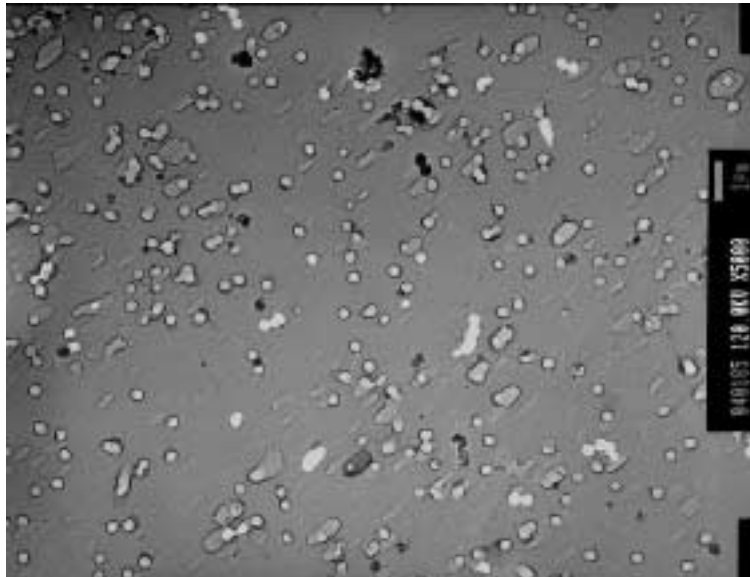


Figure B11 - Typical image from TEM of PM_{Total} for No. 2 fuel at 5000 magnification

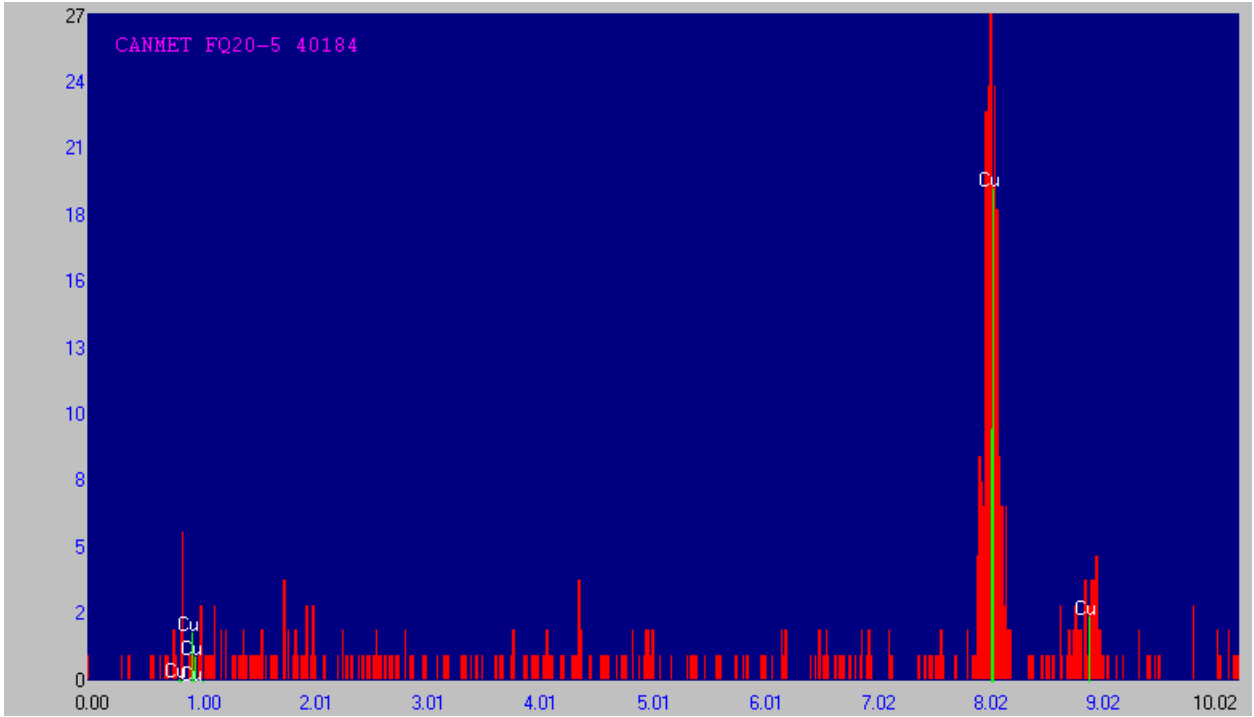


Figure B12 - Typical elemental spectrum of PM_{Total} agglomerate for No. 2 fuel

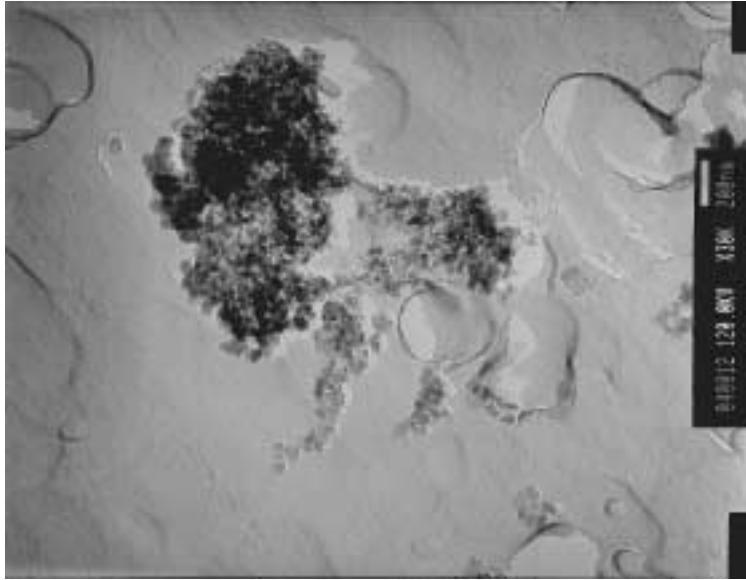


Figure B13 - Typical transmission electron micrograph of PM_{2.5} agglomerate for LD-6000 fuel at 30,000 magnification

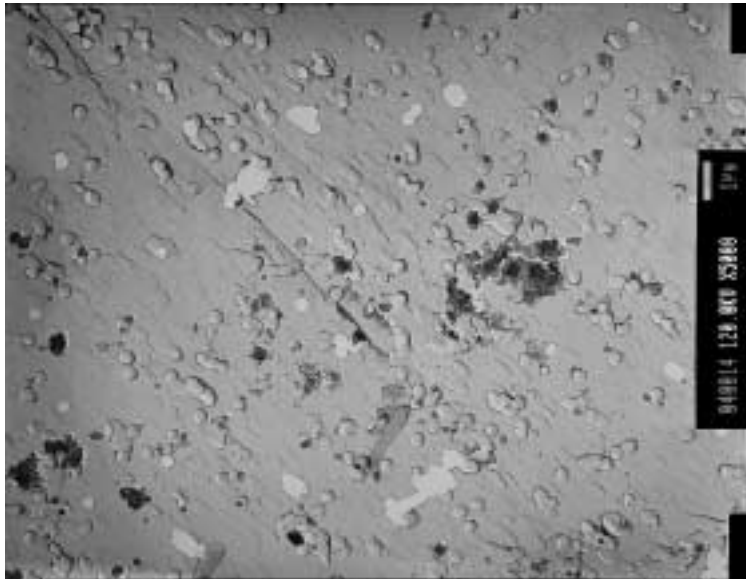


Figure B14 - Typical image from TEM of PM_{2.5} for LD-6000 fuel at 5000 magnification

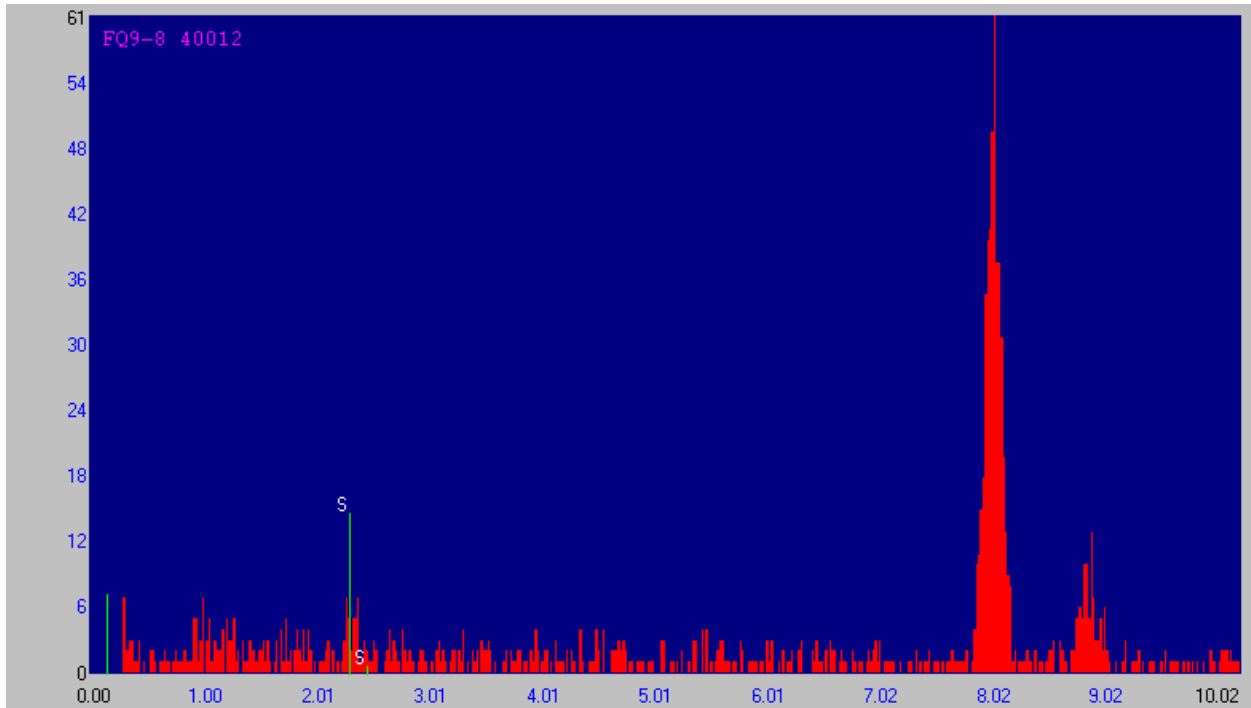


Figure B15 - Typical elemental spectrum of PM_{2.5} agglomerate for LD-6000 fuel

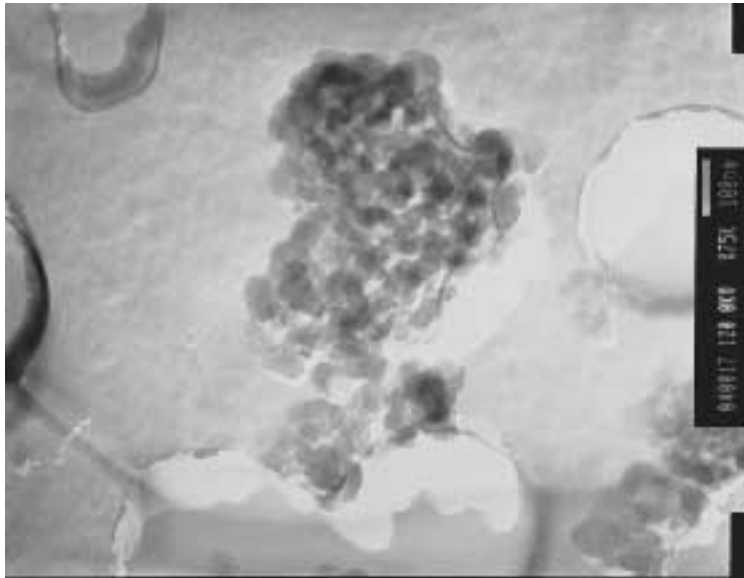


Figure B16 - Typical transmission electron micrograph of PM₁₀ agglomerate for LD-6000 fuel at 75,000 magnification



Figure B17 - Typical image from TEM of PM₁₀ for LD-6000 fuel at 5000 magnification

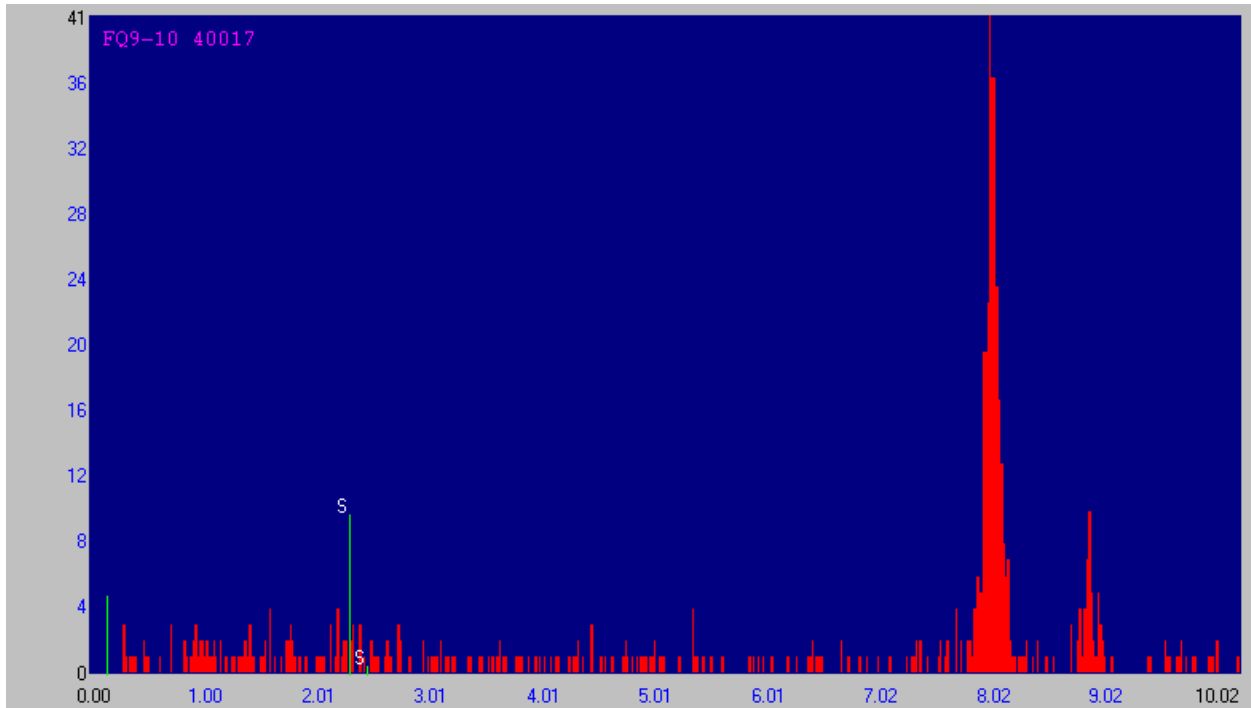


Figure B18 - Typical elemental spectrum of PM₁₀ agglomerate for LD-6000 fuel

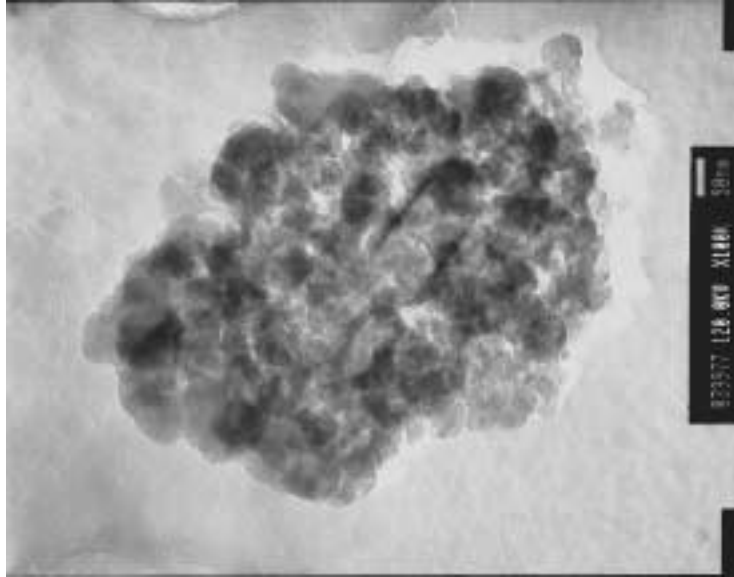


Figure B19 - Typical transmission electron micrograph of PM_{Total} agglomerate for LD-6000 fuel at 100,000 magnification

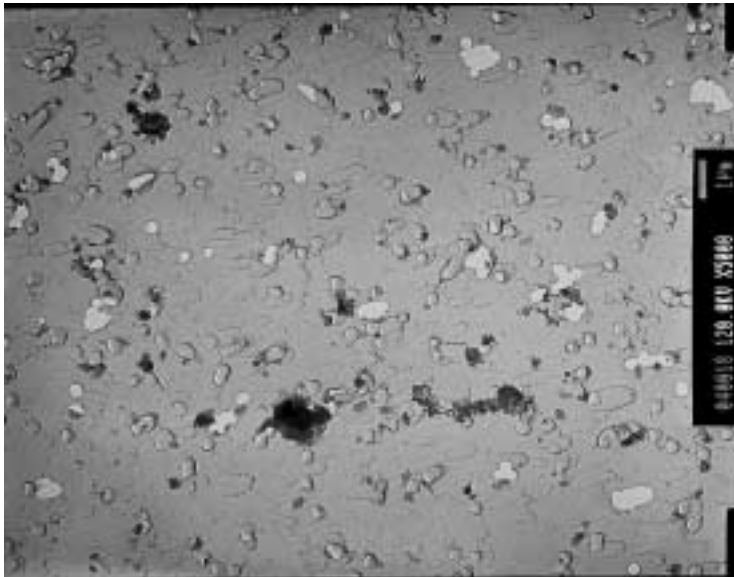


Figure B20 - Typical image from TEM of PM_{Total} for LD-6000 fuel at 5000 magnification

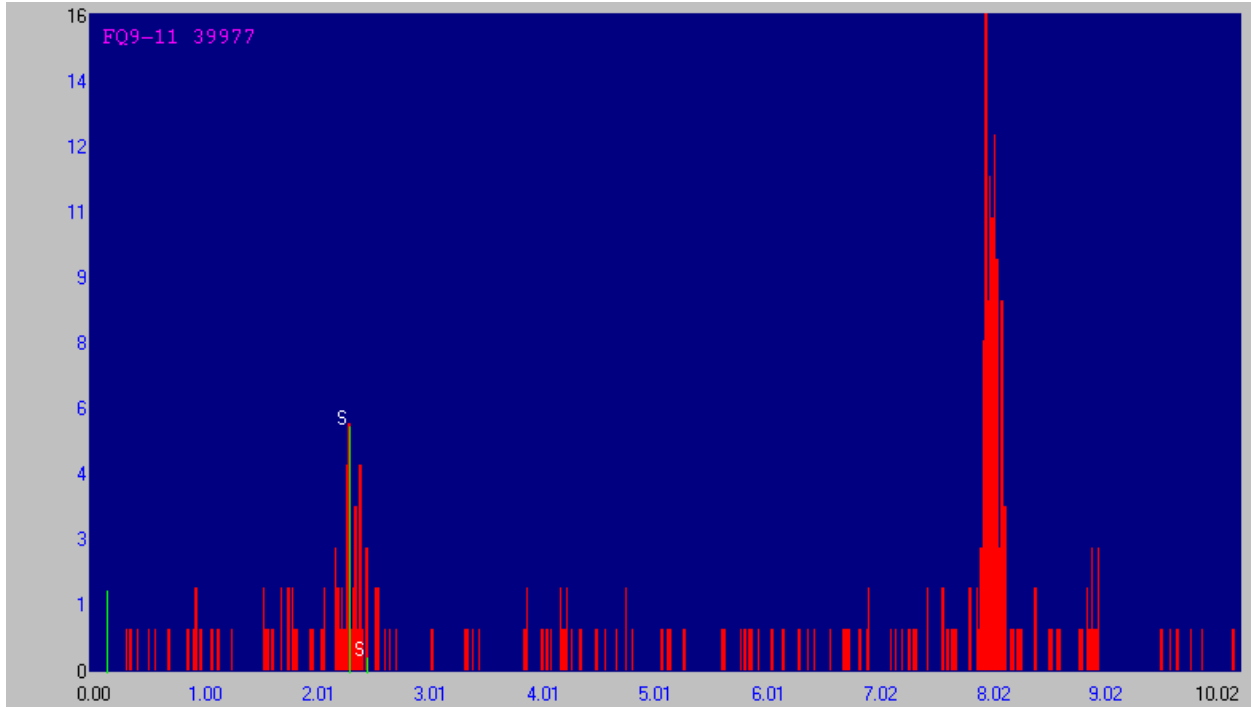


Figure B21 - Typical elemental spectrum of PM_{Total} agglomerate for LD-6000 fuel