

Diesel particulate characterisation by vacuum microbalance techniques

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Abstract

The physical and chemical character of diesel particulate (DP) has been determined. Electron microscopy (EM) and a gravimetric BET method (BET) determined particle size and specific surface area (SSA). Two different diesel engine types (direct injection (DI) and indirect injection (IDI)) were run at similar operating conditions and DP was collected by filtration of the exhaust gas at temperature without dilution.

An in-vacuo gravimetric thermal degassing (TD) apparatus has been constructed to extract adsorbed hydrocarbon volatiles from the DP during a slow heating program. The desorbed volatiles were trapped and analysed by gas chromatography (GC). The carbons were fuel- and oil-derived unburnt hydrocarbons (UHC), trapped within the slit-shaped micropores and 'ink-bottle'-shaped mesopores/surface of the aggregated diesel particles.

INTRODUCTION

Diesel engine combustion produces emission products, which include partially pyrolysed or unburnt hydrocarbons (UHC) which may adsorb onto diesel particulate (DP) which is co-formed. The UHC include some potentially carcinogenic hydrocarbon species, e.g. polyaromatic hydrocarbons (PAH's) [1]. The physico-chemical interaction between DP and UHC has been studied, so that engine manufacturers, environmental scientists and emission legislators might further understand exhaust processes and assess health risks.

The character of DP and UHC has been reported previously [2]. DP are carbonaceous particles, varying in size from 5 to 100 nm in diameter (for incipient to aggregated particles) and possess a complex microporous and

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aggregate structure. UHC adsorption during formation depends on engine load. Low engine load produces 'fuel-rich' conditions and the DP formed is 'saturated' with UHC trapped in the slit-shaped micropores (< 2 nm diameter) thus giving soots of low SSA (< 20 m² g⁻¹). High load conditions have high DP production and 'fuel-lean' conditions and, therefore, less UHC is trapped in the micropores and SSA values are higher (up to 100 m² g⁻¹). In the exhaust, temperature controls UHC adsorption to the 'ink-bottle' mesopores (2–50 nm diameter) and macropore/surface (> 50 nm). This UHC adsorption only slightly decreases SSA but enlarges particle size and encourages particle aggregation to form large fluffy structures [3]. The UHC collected by the filter, at temperature and extracted by any method, is termed filter-extracted sample (FES).

A previous study [2] identified the exhaust process, termed temperature-dependent chemical scavenging (TDCS), and examined how DP SSA varies between engine conditions, for ultrasonicated soots. These were then subjected to TD which desorbed the FES, opened the pores and increased SSA. Unfortunately, the volatiles could not be collected. Thus an in-vacuo evolved-gas analysis (EGA) system has been constructed to trap the desorbing FES for analysis by gas chromatography. This method offers the advantages of a fast solvent-free extraction without fibre contamination [4].

EXPERIMENTAL

The engines used were a single-cylinder Ricardo E6/T with a Comet Mk 5 IDI head (compression ratio 22:1, cylinder volume 0.5 l) and a pre-production four-cylinder Ford DI (compression ratio 19:1, cylinder volume 2.5 l) engine. The engines were preconditioned for 1 h (full speed and load) before being stabilised to the required engine state of 1500 rpm and full load (27.4 and 84.2 Nm respectively). Filter samples were taken at 3.3 m down an exhaust of 4.2 cm. i.d. DP, filtered using a specifically designed unit was collected on Pallflex TX-40, teflon/borosilicate glass fibre filters. The mass loading was determined by the filter weight gain measured after equilibration in a humidity box (Rh 60%). The exhaust gas volume of the DI engine limited the filter to 3/4-full exhaust flow.

Electron micrographs were taken of the fresh DP. Specific surface area (SSA) and pore character were determined on-filter by a gravimetric BET N₂ adsorption technique [5]. The TD apparatus (Fig. 1) degassed DP on-filter. A CI Electronics Mk II balance head used for the BET method was adapted to accept a glass sample envelope (with a Pt/Rh 13% thermocouple to monitor temperature), around which a heating furnace could be raised. The filter sample was suspended, and a cold trap filled to be within 4 cm of the sample. The apparatus was evacuated to 1 mm Hg pressure to remove those volatiles with an appreciable vapour pressure at room temperature (mainly water). Liquid N₂ was added to the cold-trap dewar and the

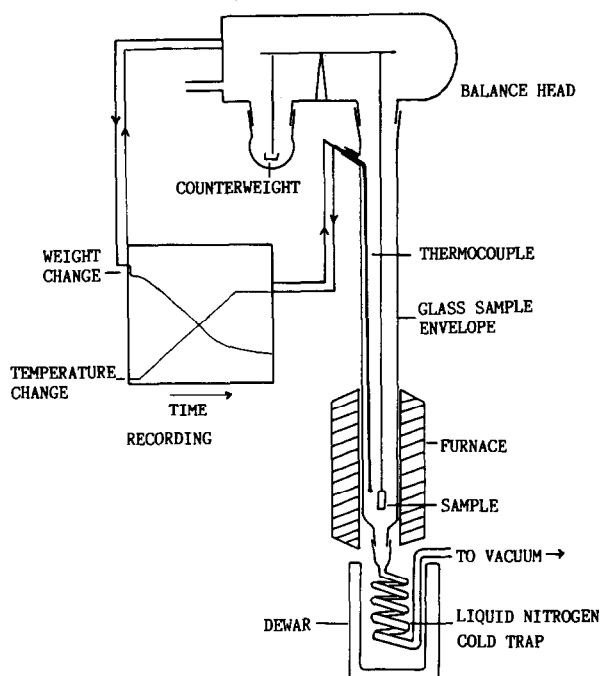


Fig. 1. The thermal degassing apparatus for extracting volatile FES from diesel particulate (DP). The apparatus was operated at 1 mm Hg pressure and samples were thermally degassed (TD) at 320°C.

temperature program initiated (approx $5^{\circ}\text{C min}^{-1}$ to 320°C). Weight and temperature changes were recorded on a couple chart recorder. Samples could be degassed at preset temperatures, the volatiles collected and microstructure re-examined.

A Carlo Erba HRGC 5360 equipped with cold on-column injection and an FID, was employed to analyse the volatiles removed from the trap with dichloromethane (DCM). The DCM-soluble FES was reduced in volume (rotary evaporation, 30°C) and transferred quantitatively to a preweighed vial (1.75 ml); N_2 was used to blow down to dryness, thereby giving a dry FES mass. The injection volume was $0.1 \mu\text{l}$ and sample concentration 10 mg ml^{-1} .

RESULTS AND DISCUSSION

Filtration and filter influences

During this investigation, we attempted to obtain, for all engine conditions, a DP mass loading sufficient for mechanical removal from the filter. With the exception of the sample in Fig. 2, which was an over-fuelled, high-load sample (thus giving exceptional DP production), this was found

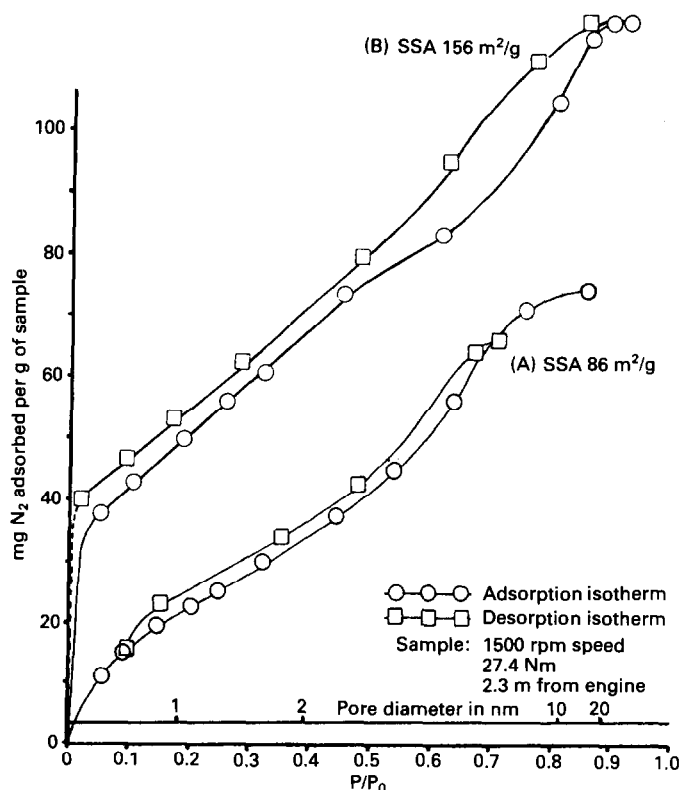


Fig. 2. Adsorption/desorption isotherms and hysteresis loops of a DP brushed from a filter exposed to the exhaust of the Ricardo IDI engine. The figure shows the sample before (A) and after (B) thermal degassing.

to be impossible. This was due to filter matrix burial and low DP mass loadings. Therefore, on-filter techniques were developed.

Figure 2 shows a DP structure which is characteristic of a non-compacted exhaust soot, showing a cross between IUPAC Type II and Type IV isotherm [6], suggesting a semi-porous solid. The hysteresis profile is largely H3, typical of silt-shaped platelet microstructure, but with some H1 influence ($>0.8P/P_0$). This suggested that the aggregate particles produced 'ink-bottle' pores between them. The EM particle size analysis showed a mean particle size distribution of 30–40 nm which nearly correlated with the H1 point of influence ($>0.93P/P_0$). TD opened the micropores (<1 nm) and mesopores (>8 nm) with the SSA increased from 86 to 156 m² g⁻¹. Unfortunately, this sample was analysed before the trapping system had been developed and no FES was collected.

The mass and density of buried DP and filter must be accounted for in the assessment of SSA. The SSA value, calculated using the BET method [5]

and used for carbons by Carter [7], was corrected using eqn. (1), assuming a filter X-ray density of 2.08 g cm^{-3} and a filter SSA of $2.47 \text{ m}^2 \text{ g}^{-1}$ ($\pm 5\%$)

$$\text{DP SSA} = \frac{S_1 - (S_2 M_2)}{M_1} \quad (1)$$

where S_1 is the SSA value calculated from the BET equation, S_2 is the SSA of the filter ($2.24 \text{ m}^2 \text{ g}^{-1}$), M_1 is the particulate dry mass divided by dry sample mass, and M_2 is the filter dry mass divided by dry sample mass. The sample mass is the sum of the filter and DP mass.

The filter showed hysteresis in all pore ranges. The influence of this on the DP isotherms was to ‘flatten’ the isotherm profile and to give a permanent open microstructure; thus on-filter samples never show micropore closure, even when significant soot was present and microporous gain was noted.

Compositional analysis on DP on-filter

DP, from the two engines showed characteristic differences (Fig. 3). The engine type influenced the DP emission but not the UHC output [8]. The IDI engine produced high DP emissions due to its relatively inefficient design and pre-chamber ‘fuel-rich’ combustion. Thus FES represented 9% of DP mass and gave an initial SSA of $109 \text{ m}^2 \text{ g}^{-1}$. The DI engine produced less DP from its four cylinders, as one would expect from a modern DI engine, but had low SSA ($1 \text{ m}^2 \text{ g}^{-1}$) and 61% FES of DP mass. This was higher than expected, reflecting that the SSA of the DP was more suppressed when the low DP mass adsorbed the high quantity of UHC present.

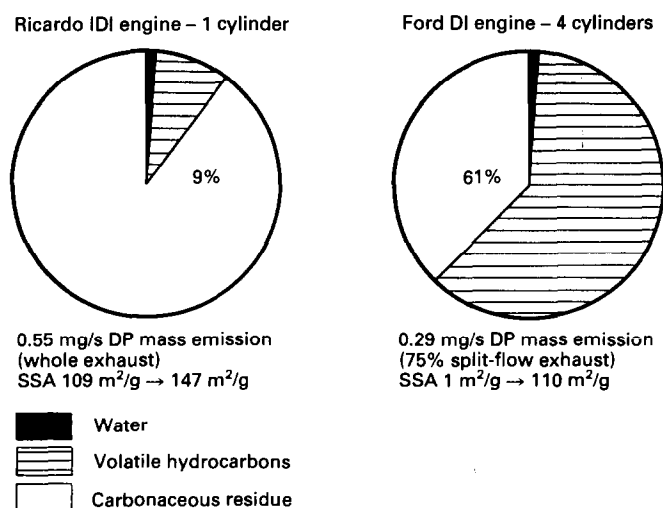


Fig. 3. Pie graphs of composition of DP collected from the exhausts of the two engines. Also shown in the specific surface area (SSA) before and after thermal degassing (TD).

EGA and microstructural characterisation of DP on-filter

The microstructure, before (A) and after (B) TD, and degassed volatile FES chromatograms are shown in Figs. 4 and 5, for the IDI and DI engines respectively. Both samples showed H3 slit-shaped pore character (modified by filter hysteresis with a ‘flatter’ profile and no closed micropores), but no H1 influence because compaction and filter burial had destroyed the ‘open’ agglomerate structure. TD of DP opened the pores, with a gain in SSA that was great for the DI sample because of its high FES content. Analysis of the chromatograms showed that both samples contained an unknown complex mixture (UCM) of branched hydrocarbons and polar compounds, which correlated with the retention time of lubricating oil. An *n*-alkane series of peaks was also evident (identified by co-injection of standards) which corresponded to the higher molecular weight hydrocarbons left after combustion of the fuel.

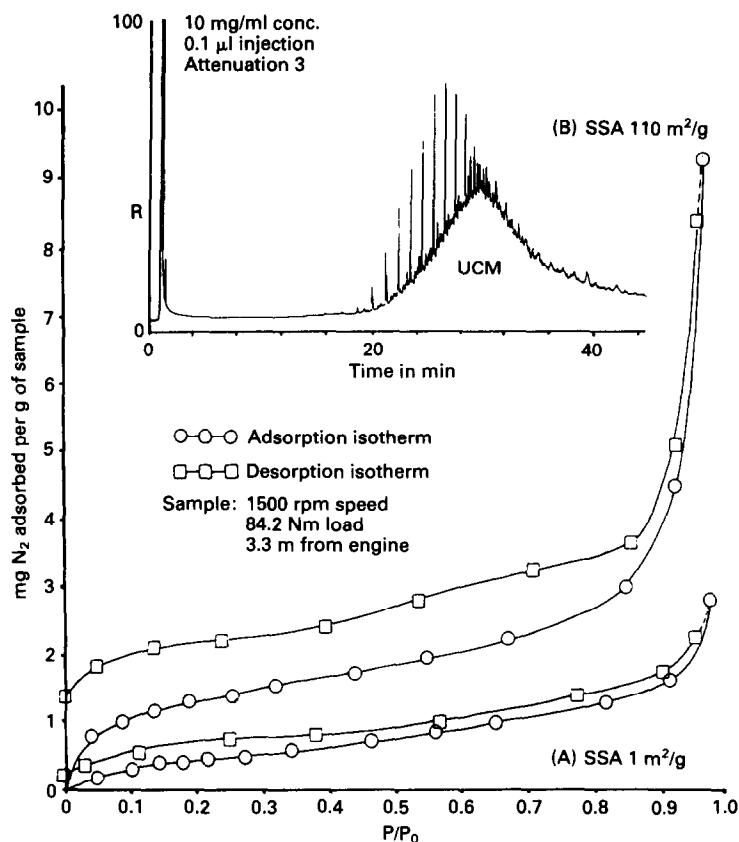


Fig. 4. Adsorption/desorption isotherms and hysteresis loops of a DP collected from the exhaust of the Ricardo IDI engine. The figure shows the chromatogram of the volatile FES and the microstructure before (A) and after (B) thermal degassing.

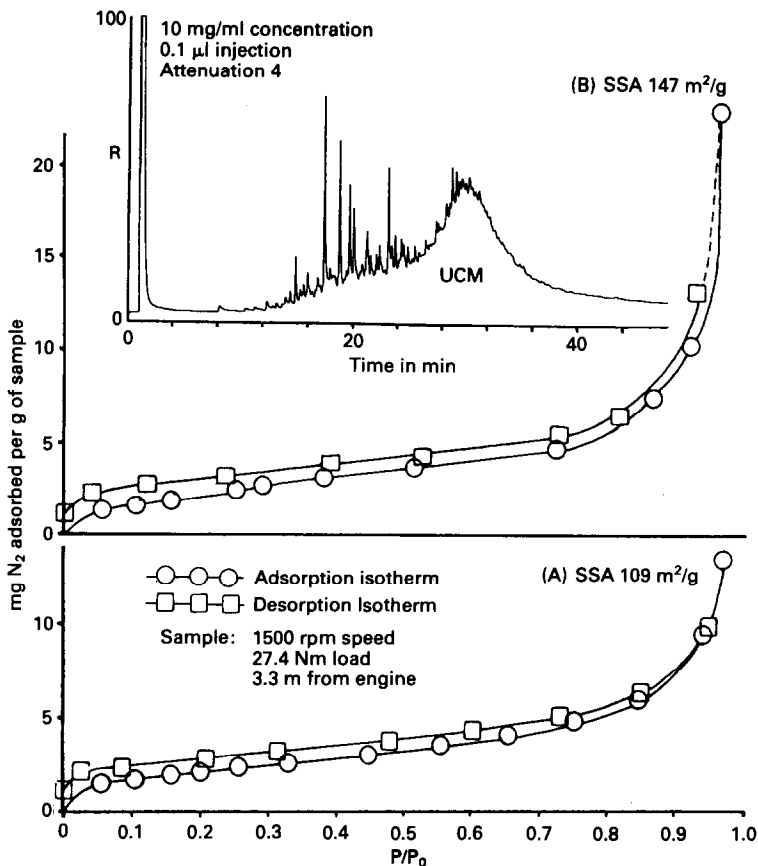


Fig. 5. Adsorption/desorption isotherms and hysteresis loops of a DP collected from the exhaust of the Ford DI engine. The figure shows the chromatogram of the volatile FES and the microstructure before (A) and after (B) thermal degassing.

CONCLUSIONS

The vacuum microbalance technique is advantageous over conventional carrier gas methods because of its more efficient quantitative removal of higher boiling point UHC at lower temperatures. This reduces the possibility of decomposing the volatiles and of changes in the DP by microstructural thermal swelling. The technique also permits determination of the changes in surface area and porosity of the DP on progressive removal of volatiles.

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