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# Influence of High Injection Pressure on Diesel Fuel Stability: A Study of Resultant Deposits

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## ABSTRACT

Recent developments in diesel engines and fuel injection equipment together with the move to ULSD and bio-blends have seen an increase in reports regarding deposits in both injectors and filters.

Historically deposits have been generated from a number of sources: bio-contamination, both aerobic and non-aerobic, water contamination, lube oil adulteration, additives, dirt, metals in fuel, and biodiesel degradation. These may be ascribed to "poor housekeeping," incorrect additivation, deliberate adulteration or some combination.

However the recently observed deposits differ from these. The deposits are described and indicate possible precursor molecules that support proposed mechanisms and their ability to form filter deposits.

## INTRODUCTION

Since the industrial revolution in the late 18<sup>th</sup> and 19<sup>th</sup> century there has been a period of evolution. The rate of evolution has not been constant with periods of rapid change, interspersed with more gradual development. The automotive world is a prime example. In the later part of the 20<sup>th</sup> century many of these periods of rapid evolution have been driven by the need to meet forthcoming legislation.

For engine technology the desire for more power and efficiency has been a constant driver and has been

behind the gradual evolution of the internal combustion engine. Superimposed on this has been successive tightening of emission standards. But as these engines require fuel then in general the fuel has evolved in line with the engine.

Considering diesel fuel, the topic of this paper, there has been an evolutionary rise in the cetane number of the fuel as this allows engines to be designed for greater specific power output. Because there is usually a cost penalty associated with increasing the cetane number of the fuel, the required cetane number of the fuel varies from region to region and country to country. However, there is a trend towards convergence of specification.

Emissions legislation is also driving fuel specification towards convergence on permissible levels of sulphur in the fuel. Whilst sulphur emissions are not themselves regulated, sulphates contribute to particulate matter emissions, and more importantly sulphur can contribute to the reduction in efficacy of exhaust after-treatment devices (1-4).

To achieve these low sulphur levels the refinery usually employs a hydro-treatment process whereby the hydrocarbon stream is mixed with a hydrogen rich gas, the mixture then passing over a catalyst. The hydrogen then reacts with the sulphur compounds to produce hydrogen sulphide gas, which is then separated from the liquid hydrocarbon. This process also removes excess nitrogen, metals, and halides from the fuel (5, 6). An additional consequence of this process is that it tends to

convert unsaturated hydrocarbons, such as olefins, and particularly di-olefins, to saturated paraffins (7).

With recent concern over the so called 'Greenhouse Effect' and security of supply, there is increasing pressure to replace petroleum derived fuels with renewable or sustainable sourced products. For diesel fuel this has predominantly resulted in the inclusion of fatty acid methyl esters (FAME) as a blending component for finished diesel fuel (8). The FAME, also known as bio-diesel has many properties that are very close to those of diesel fuel.

Blends of petroleum diesel fuel and bio-diesel are denoted as Bxx, where xx represents the percentage by volume of the FAME in the finished blend. Thus a B20 is 80% volume petroleum diesel fuel, plus 20% volume FAME. B0 is pure petroleum diesel fuel, and B100 is 100% FAME. Whilst some engines can run without modification on B100 it is considered that the legacy fleet is best served with blends of no higher than B5. Cost and availability of the FAME are often the limiting factors to the uptake of these blends (9-13).

The recent change in the US diesel fuel specification to limit fuel sulphur to 15 mg/kg (14) has coincided with the inclusion of bio-diesel into the blending pool.

Over a similar time frame there has been an increase in the reported incidences of severe fouling of diesel fuel filters, and of diesel fuel injectors. These deposits appear to be more carbon like and more granular than deposits seen previously. Historically, deposits have been generated from a number of sources: bio-contamination, both aerobic and non-aerobic, water contamination, lube oil adulteration, additives, dirt, metals in fuel, and biodiesel degradation. These may be ascribed to "poor housekeeping," incorrect additivation, deliberate adulteration or some combination (15, 16). As yet there is no clear correlation between these incidences of severe fouling, and engine type, fuel injection equipment, fuel filter type or fuel supply source. However, newer technology engines e.g. those with high pressure fuel injection (HPFI) equipment, do seem more prone to problems compared with older technology.

To meet successive tightening of emission standards, diesel engine manufacturers have striven to improve the combustion process within the engine. This has called for better mixing of the fuel and air to reduce the amount of combustion that takes place in fuel rich regimes. Generally, this can be achieved by improving fuel atomisation and penetration into the cylinder from the fuel injectors (17, 18). Reduction in fuel injector hole size, and an increased fuel pressure at the point of injection, has been fundamental in this progression (19, 20). It has been suggested that these engineering improvements, and the resultant high pressures and concomitant high temperatures, contribute to the observed fouling problem by accelerating the aging of the fuel.

This paper describes preliminary work carried out to try and characterise the deposits currently being encountered in the field, and to identify possible deposit precursors.

## EXAMPLES FROM THE FIELD

In the US the incidence of fouled fuel filters is quite widespread. A number of samples were therefore collected, covering a variety of geographic locations, as well as equipment type.

A typical example of a fouled filter is shown in the upper part of Figure 1. The lower part of the figure shows a used filter that still exhibits acceptable performance.

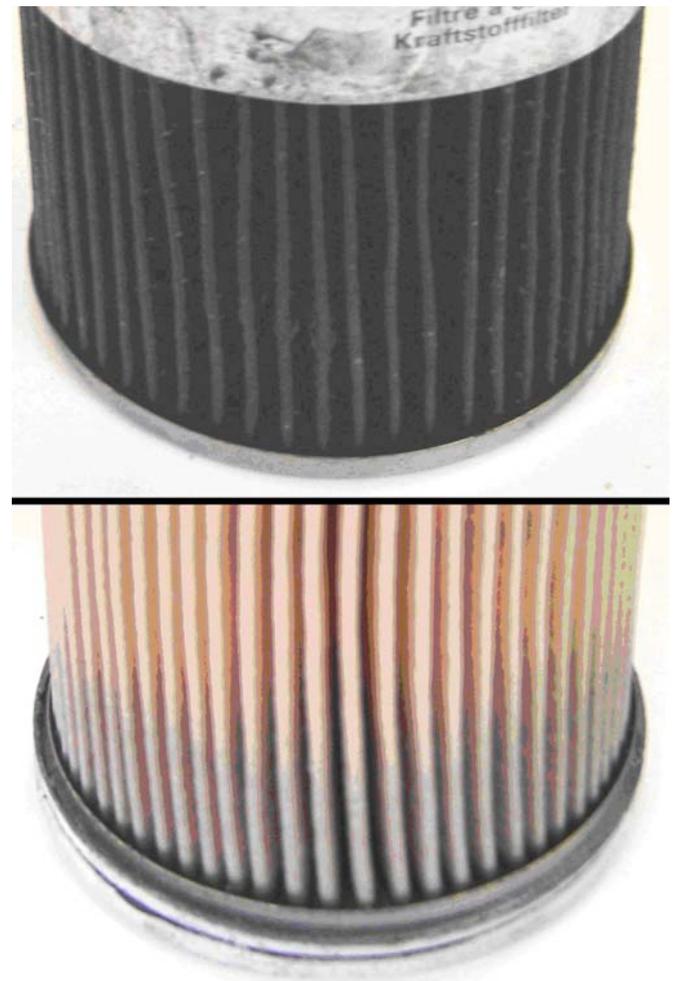


Figure 1. Typical filters taken from the field. Fouled filter above and acceptable filter below.

As can be seen from the above figure, the acceptable filter is still of a pale colour closely matching an unused filter whilst the fouled filter element is uniformly covered in a black deposit. This is further illustrated in Figure 2 which shows a section of the filter element that has been removed for analysis.



Figure 2. Typical example of a section of fuel filter

A number of fuel injectors were also analysed. A typical example of the deposits formed around the injection holes is shown in Figure 3. Although there is clearly a significant accumulation of deposit around the hole, the topography suggests that at some time there was an even greater amount of deposit. This accumulation has then become detached and fresh deposit has begun to accumulate in the cleared area adjacent to the hole.

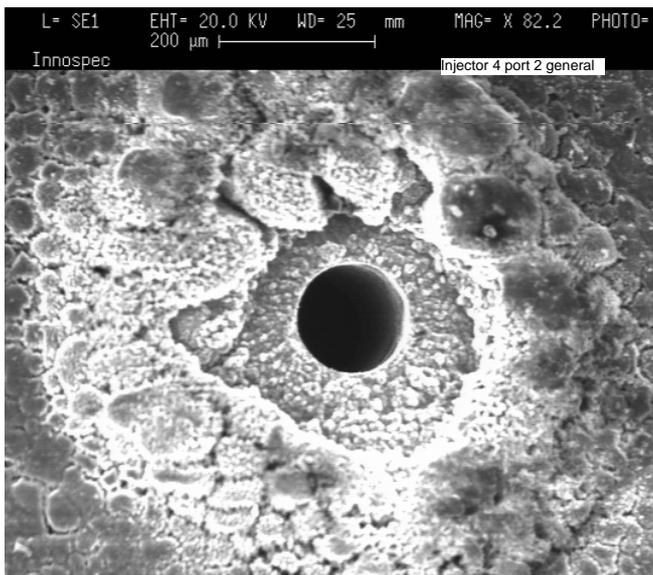


Figure 3. Deposits around injector hole.

## EXPERIMENTAL TECHNIQUES

Many of the fuel filters presented for analysis were “fuel wet”, and the following protocol was followed to enable the separation and characterization of both the soluble and insoluble moieties. The protocol is illustrated schematically in Figure 4.

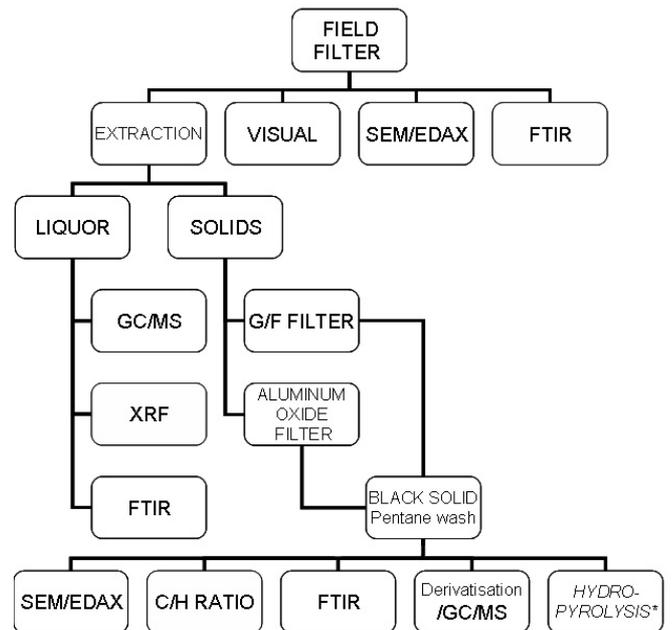


Figure 4. Analytical Separation Protocol.

A 15cm by 3cm section of the filter element was cut from the filter, an example of which is shown in Figure 2. A gravimetric evaluation of this filter section was made, to allow a determination of residue levels. The filter section was then subject to visual analysis, scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDAX), and Fourier Transform Infra-red analysis (FTIR). The deposit was then extracted with 120mL of HPLC (High Pressure Liquid Chromatography) grade tetrahydrofuran, either by 15 minutes in an ultrasonic bath, or an overnight soak. The liquor was then filtered through an 8 micron glass fibre filter, or a 0.2 micron aluminium oxide membrane. The filtrate was washed in pentane to remove any remaining diesel fuel, and subjected to SEM/EDAX, carbon/hydrogen ratio analysis, FTIR, derivatised gas chromatography with mass spectroscopic detection, (GC/MS), and hydropyrolysis (21). The filtered liquor was then subject to (GC/MS), X-ray fluorescence (XRF) and FTIR.

The results of the various analyses are given in the following sections.

## RESULTS OF SEM/EDAX FTIR ANALYSIS

**SEM/EDAX ANALYSIS** - In order to assess the filter deposits before chemical extraction was carried out, SEM/EDAX analysis was performed on a strip of filter cut from the original filter housing. Figure 5 shows a SEM image that clearly demonstrates the granular deposits adhering to the fibres that make up the filter material.

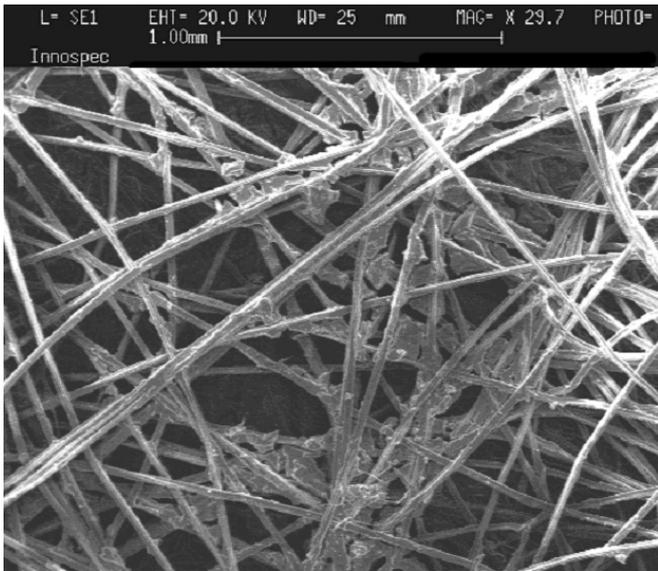


Figure 5. Original field filter

Figure 6 shows a SEM image of an agglomerate of this deposit that has been removed from the filter. The EDAX analysis confirmed that these deposits were mainly organic.

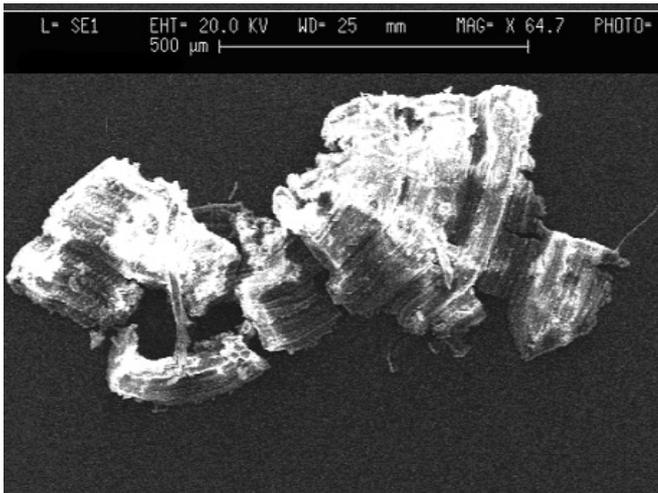


Figure 6. SEM of black particle

Figure 7 shows a SEM image of the filter. In this image, the granular particles are clearly visible. However, they are trapped in an organic film that is coating the filter.

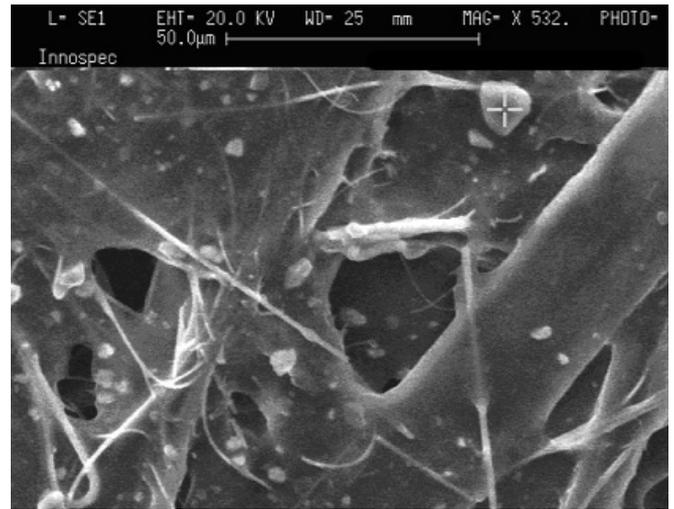


Figure 7. Original Field Filter

Figure 8 shows a SEM image of the filter showing the deposit with the polymeric organic film. This image is of particular interest as it shows the filter to be blocked with a combination of solid particulate and polymeric organic material that has been “filtered” from the diesel fuel. The number of filter pores available is significantly reduced by the carbon particles. Dispersants are added to the diesel fuel to act as detergents and maintain the cleanliness of the fuel injection equipment. These dispersants are designed to have an affinity to deposits and thus hold them in a dispersion within the fuel. Thus, if deposits are sufficiently large and/or numerous to be trapped in the filter, then the dispersant will tend to be collected with them. Historically, this has often resulted in a preliminary analysis showing the presence of fuel additive, with the subsequent erroneous conclusion that it is the additive that is causing the blockage problem.

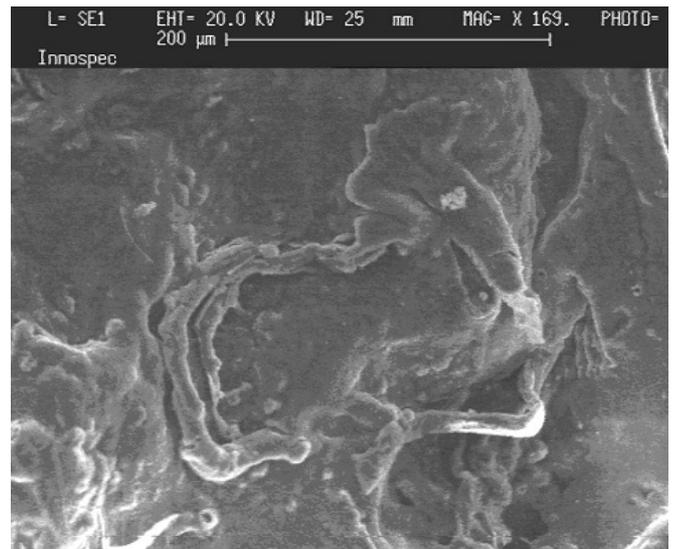


Figure 8. Original Field Filter

The weight of material taken from the filters is listed in table 1. The table gives the total weight of the residue

removed, i.e. the weight of the strip of filter before extraction minus the weight of the strip after extraction. The table also shows what percentage of the residue removed was black solid, i.e. the amount of material that is left after the extracted liquor has been filtered and washed.

Table 1. Gravimetric analysis

Filter #	Weight of residue (g/g of filter)	Proportion black solid (% m/m)
1	0.47	1.5
2	0.71	8.6
3	0.44	1.2
4	0.61	2.7
5	0.57	4.6

The table shows that despite the high loading density (expressed as grams of residue per gram of filter) only a small proportion of the residue is attributable to the granular carbon material described above.

Visually the isolated material after washing with pentane and then residual solvent evaporation in air was found to be black and granular in nature, as shown in Figure 9. Attempts to dissolve the material in common solvents methanol, acetone, tetrahydrofuran, dichloromethane and toluene, were unsuccessful. Experiments using solvents across the polarity range namely acetone, dichloromethane, toluene, and pentane as "washing" solvents to identify deposit precursors, are still being evaluated.

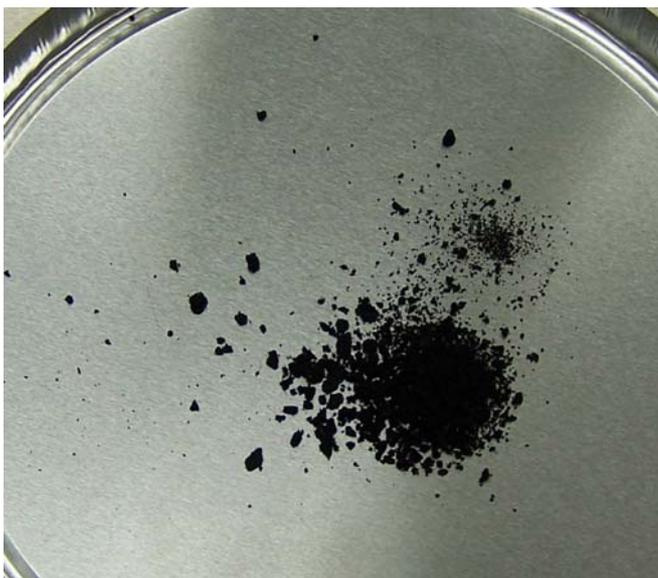


Figure 9. Isolated black solid.

Figure 10 shows a SEM image of the solid deposit. The granular nature of this material is clearly visible.

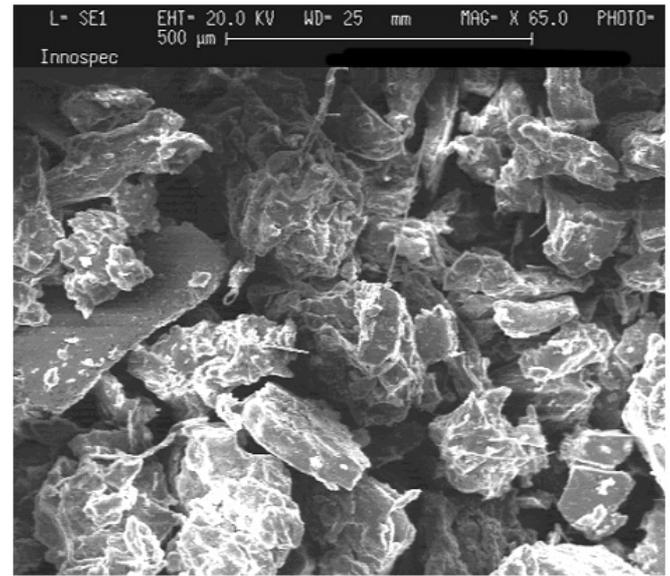


Figure 10. Isolated black solid from filter

FTIR ANALYSIS - Infra-red spectroscopy analysis of the original filter shown as figure 6 indicated as expected, mainly fuel based bands, with some functionality around  $1746\text{ cm}^{-1}$  and  $1555\text{ cm}^{-1}$ , attributable to oxygen containing species, and those around  $878\text{ cm}^{-1}$  and  $721\text{ cm}^{-1}$  attributable to aromatics. The FTIR trace is shown in Figure 11.

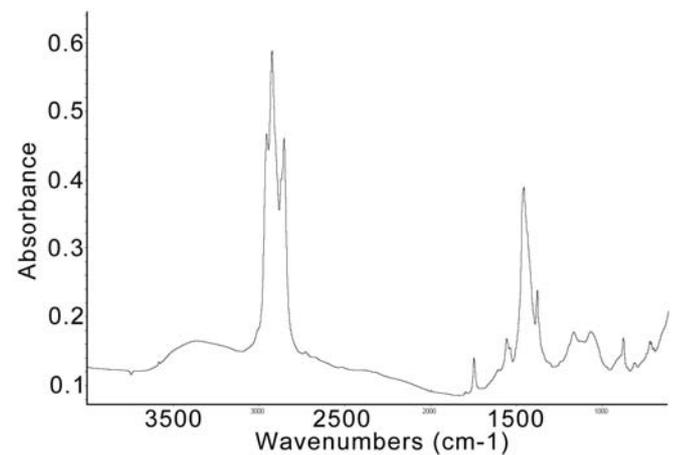


Figure 11. Infra-red spectrum of original field filter.

Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS): Diffuse Reflectance occurs when infra-red radiation impinges on the surface of a material and is partially reflected and transmitted. A spectrum characteristic of the sample arises from radiation penetrating into the interior of the sample and re-emerging numerous times. Selected wavelengths of the infra-red radiation are absorbed and the spectrum produced yields information regarding chemical groups present.

DRIFTS is a useful technique for analysis of solids. Figure 12 shows the DRIFTS spectrum for the isolated solid that is shown in Figure 9.

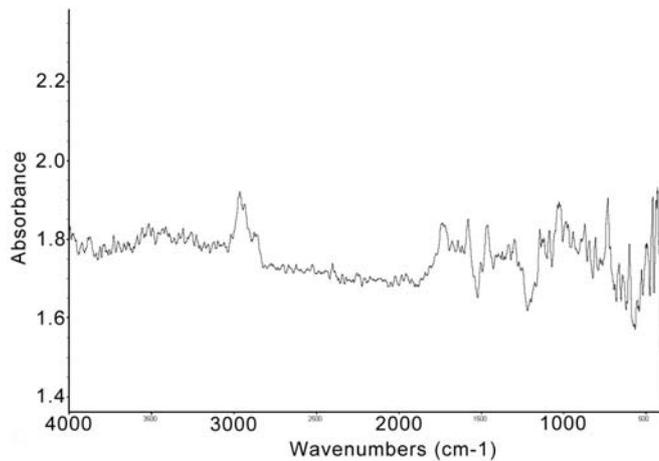


Figure 12. The DRIFTS spectrum of the black solid isolated from the filter as shown in figure 9.

The weakness of the DRIFTS signal is indicative of high carbon content, although some fine structure functionality is present, with bands at  $1734\text{ cm}^{-1}$  indicating C=O and at  $1206\text{ cm}^{-1}$  indicating C-O. Aromatics are indicated by the bands between  $700\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$  (22).

**ELEMENTAL ANALYSIS** - The H/C ratios determined for the isolated residues varied from 1.82 to 1.24. In the refinery industry, coke formation is a known phenomenon (23). However, the H/C ratios found in these fuel filter residues were very different from those found for refinery 'popcorn coke' (0.65-0.75). This 'popcorn coke' is formed in units processing coker volatile liquid product by a polymerization mechanism. They are also significantly different from thermal coke; formed from thermal cracking; (0.20-0.45). This is indicative of the carbon being present as a mixture of graphitic and organic species, as the infra-red data has indicated, with oxygenated organics and aromatics being part of this matrix. The absence of zinc and phosphorus in both EDAX and XRF was taken as indicative of the absence of lubricating oil adulteration of the parent fuel. Thermal analysis of typical residues indicated that approximately 12% was inorganic. The EDAX analysis indicated that the filter material contained metals, e.g. calcium and iron. The infra-red spectrum shows no evidence for salt formation in the solid taken from the filter.

## RESULTS OF GC/MS ANALYSIS

This will be described in three parts:

1) The application of GC/MS to the liquor residues yielded data shown in figure 13.

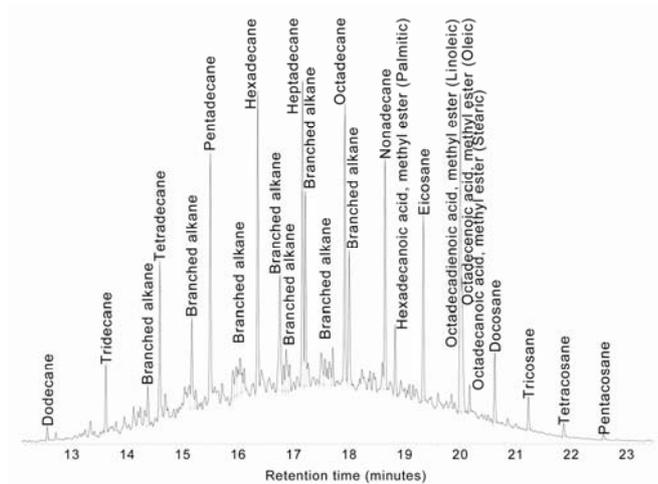


Figure 13. GC/MS of filter liquor.

The data indicates alkanes from the diesel fuel as well as the methyl esters of palmitic, linoleic and oleic acid, but no substituted aromatics or alkenes which may point to them as carbon precursors in the fuel.

2) The application of derivation chemistry (methylation of components possessing organic acid/ester functionality) to permit GC/MS analysis of the filter solids.

It is clear that these solids, although mainly carbon also have some functionality present from the DRIFTS IR spectrum described in figure 12, and these organic molecules may prove to be possible precursors to the final deposits. In an attempt to release these from the carbon matrix the materials were derivatised with trifluoro-boron/methanol ( $\text{BF}_3/\text{MeOH}$ ) and GC/MS analysis carried out. An example of the resulting GC/MS trace is shown in Figure 14

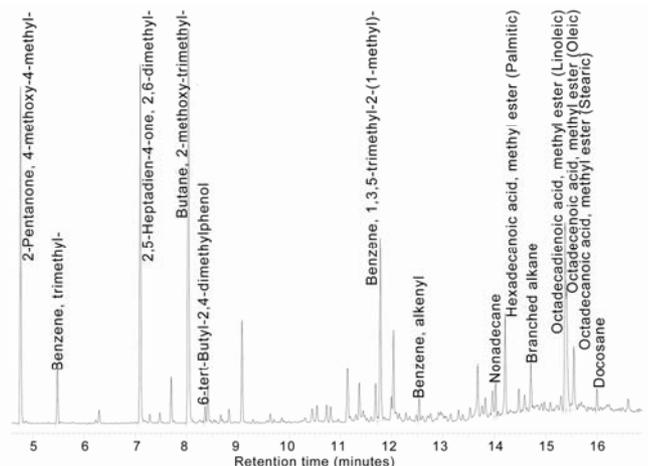


Figure 14. GC/MS of derivatised black solid isolated from the original filters.

The presence of ethoxyethenes, acids and alkene substituted benzenes which are all possible candidates for precursors (24-26) was noted. Interestingly, several residues were found to contain C16-18 acids

(derivatised to their corresponding ester). Furthermore, the application of the technique of hydrolysis GC/MS to the residues, again yielded evidence for significant C16-C18 backbone presence in the residue.

### 3) Good Fuels Bad Fuels:

Preliminary GC/MS analysis of a set of fuels, known to cause deposits within injector and/or fuel filters, was carried out. An example of the GC/MS traces produced is shown in Figure 15.

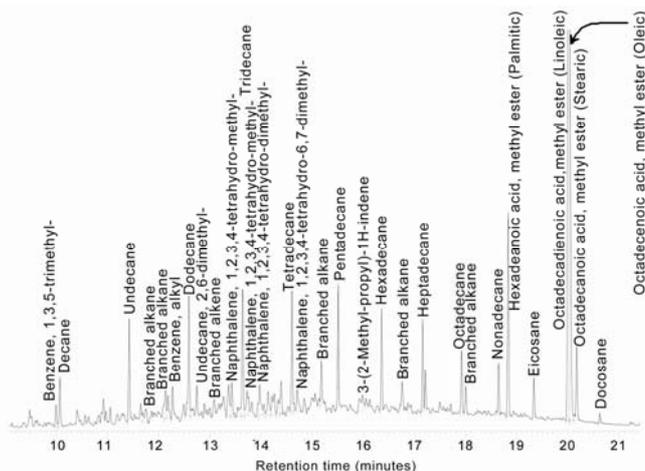


Figure 15. GC/MS of example fuel

The GC/MS data was normalised by taking the area under individual peaks as a percentage of the total area. The profile results from this analysis are summarised in Table 2. For the B20 blend a second set of results was determined for only the pure hydrocarbon based data. Table 2 shows a number of deposit precursor possibilities, from alkenes to substituted aromatics, but not a sufficiently significant difference, to allow us to attribute one of these sets to coking issues.

The major observation is that both straight ULSD (B0) and biodiesel blends (Bxx) can cause this issue to occur.

Table 2. GC/MS Summary of fuel components.

Sample	Alkane	SUB alkane	SUB benzene	SUB Napthalanes	SUB alkenes	Others	Carbon
ULSD1	52.35	22.76	4.98	19.91			No
ULSD2	47.63	25.22	21.51	5.64			forms
ULSD3 (B20)	28.59	10.89	1.57	4.83	3.78	50.34	forms
ULSD3 HC only	57.6	21.9	3.16	9.7	7.6		
ULSD4	42.62	30.11	11.49	6.05	9.73		forms
ULSD5	52.29	15.77	13.70	7.47	10.77		No
ULSD6	38.54	17.56	19.84	7.58	14.74	1.74	No

## DISCUSSION

This preliminary data indicates filter and injector deposits to be mainly carbon. The trace of functionality which is present may be attributable to some oxygenated species especially C16-C18 acids. Analysis of the fuels indicates that the cause is independent of whether a biodiesel blend or straight run ULSD is being used. This may be because of some, as yet undetected factor in fuels, or a result of the higher thermal and pressure loads that the fuel is subjected to, as a result of fuel injection equipment.

## CONCLUSION

The introduction of ULSD, biofuel blending components, and modern diesel engine technology, has led to a rise in the incidence of fuel filter and injector fouling. This fouling takes the form of black, granular deposits in the injector and filter systems of modern engines. These deposits are carbon in nature with C16-C18 acids/esters present. The deposits are found in the field in the presence of other materials in complex matrices.

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