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Possible Influence of High Injection Pressure on Diesel Fuel Stability: A Review and Preliminary Study

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ABSTRACT

Recent developments in diesel engines and fuel injection equipment combined with the change to ULSD and bio-blends have resulted in increased reports regarding deposits within injectors and filters.

A review of known fuel degradation mechanisms and other relevant chemistries suggests the effects of high pressure and high shear environments should be examined as the most probable causes of increasing deposit formation. Existing fuel quality tests do not correlate with reported fouling propensity. Analytical studies have shown that there are only subtle chemical changes for the materials within the standard diesel boiling range. The implications for further scientific study are discussed.

INTRODUCTION

The deposition of materials within diesel fuel injection equipment and the blockage of fuel filters by material phase-separating from diesel fuels are far from new phenomena. Previously identified causes include [1]:

- Fuel adulteration with lubricant oil,
- Additive mis- or over-treatment and
- Bio-fouling.

The observed increase in the frequency of such occurrences suggests strongly that one or more recent change(s) must be responsible. A search for such

changes, based on literature precedents and an awareness of the prior issues produced four candidates:

- Increased injection pressure to meet tighter emissions requirements,
- Shear and / or resulting temperature generated within injectors,
- Increasingly severe hydrotreatment of harder to refine fuel sources and
- Incorporation of bio-derived components.

Problems have been reported for both Ultra Low Sulphur Diesel (ULSD) and bio-component containing fuels. Accordingly, whilst bio-components could be a major factor, they could not be the sole cause.

Hydrotreatment, almost inevitably required to produce ULSD, in removing fuel sulphur also reduces the concentrations of both aromatic and polar species [2]. Extraction of polar species (largely O- and N-containing) has been shown to significantly reduce deposit-forming tendencies of diesel fuel, at least under accelerated ageing (storage simulation) conditions [3]. ULSD is less polar than higher sulphur grades and so a poorer solvent for any oligomers formed from reactions of any remaining O- and N-containing species [4]. The two consequences of hydrotreatment are thus likely to have opposite effects on tendency to form deposits.

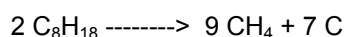
It should also be recalled that in a high pressure common rail engine fuel is released from the high pressure common rail to the low pressure fuel return line through the inlet and outlet restrictors on the valve control chamber [5]. Dependent on the pressure drop

and orifice size involved, there arises the possibility of jetting high- into low-pressure liquids, generating shear, friction and consequently heat [6]. The extent and importance of any such possible effects on fuel quality are not clear to us.

By contrast, high (greater than atmospheric) pressures are well known to accelerate a number of chemical reactions [7] in particular those with a negative volume of activation [8]. These include reactions such as the Diels-Alder, ene and carbonyl-ene [9] that involve reactants known to form as a consequence of the free radical oxidation of fuels at moderately elevated temperatures (see below). Pressures within the common-rail of diesel engine injection systems have, according to the manufacturers, been subject to an ongoing process of increase [10]. Accordingly, the inter-linked processes of fuel oxidation and deposit generation are reviewed in order to establish which classes of fuel component are the more likely to be associated with the recent increase in reports of injector fouling and filter blocking.

PROPOSED MECHANISMS INVOLVED IN DEPOSIT PRODUCTION

THERMODYNAMIC AND PRACTICAL FEASIBILITY –
In considering how carbon-rich deposits might arise from diesel fuels it is instructive to recall that the ultimate thermodynamic products of the anaerobic decomposition of carbon-based life-forms are methane and graphite. The reaction:



has a free energy change, ΔG_{298}° , of $-244.5 \text{ kJ.mol}^{-1}$; it can proceed spontaneously unless kinetic factors intervene. During anaerobic decomposition of organic matter, once the chemically bound oxygen is lost, typically as carbon dioxide, the numerous cracking, cyclisation and aromatization reactions involved in the conversion of complex hydrocarbons to deposits of coal and methane-rich gases can be interpreted as hydrogen transfer reactions necessary to the above process [11]. Diesel fuel may contain up to about 70 ppm w/w O_2 , $< 2 \times 10^{-3}$ molar [12] and this level rapidly replenishes on exposure to air [13]. There is thus scope for reactions involving both the presence and substantial absence of molecular oxygen. It is thus perhaps the rate at which deposits can form, even in the substantial absence of known deposit precursors (see below) that should be surprising, rather than that they form at all.

The stable form of molecular oxygen has two unpaired electrons. It is able to react rapidly with carbon-centered radicals whilst retaining an unpaired electron capable of abstracting a hydrogen atom, thereby forming a new carbon-centered radical. This process lies at the heart of a widely-accepted mechanism proposed to operate in jet fuels, shown in Figure 1 [14]. Based on this

mechanism a pseudo-detailed kinetic model, including Arrhenius factors and activation energies, has been developed, combined with computational fluid dynamics and applied to prediction of (measurable) oxygen consumption in heated tube experiments using jet fuel [15]. The remaining challenge to such a mechanism is to provide a fully satisfactory explanation of the initiation step. Oxidation of highly vulnerable components, such as those containing diallylic methylene groups [4] and homolysis of existing hydroperoxide [12] have been suggested. Transition-metal catalysed single electron transfer reactions have been shown to be widely-occurring and frequently to feature polar N- or O-containing species that could bind to the metals involved [16]. It would seem reasonable to suggest that the primary cause may vary between fuel samples.

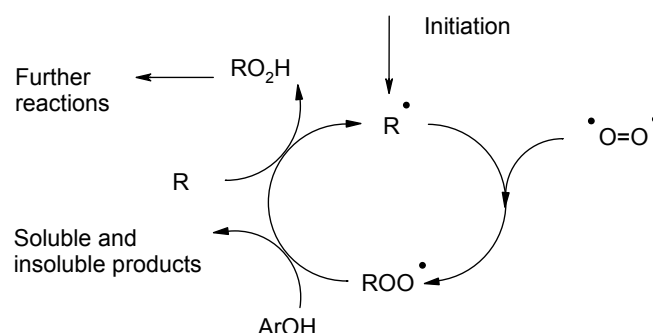


Figure 1. Summary of generally-accepted scheme for jet fuel oxidation. R represents a generic alkyl group and Ar an aryl moiety.

ALIPHATIC CHEMISTRY – Deposits arising from the low to moderate temperature decomposition of fuels have consistently proven to be resistant to characterization, even following attempts to form them from, predominantly, a single source [17]. One cause may be that any and all reactions involved in a lengthy sequence may be happening simultaneously in and on a mass of deposit [18]. A second, probable, cause must lie in the extraordinary variety of products that can arise from a single source. This is best illustrated in the case of the oxidation of hexadecane at temperatures between 120 and 190°C. Comprehensive analyses of structure, kinetics and mechanism have been provided and account for; intramolecular reactions leading to (*inter alia*) keto-hydroperoxides [19], fragmentation to yield aldehydes, olefins and carboxylic acids [20] as well as formation of cyclic ether products [21]. The original authors' summary scheme is presented in Figure 2, below.

Formation of aldehydes and ketones on oxidation of fuels at moderate temperatures may be a universal phenomenon. Such products have been identified in the exhaust from a motored gasoline engine operating on n-heptane fuel [22].

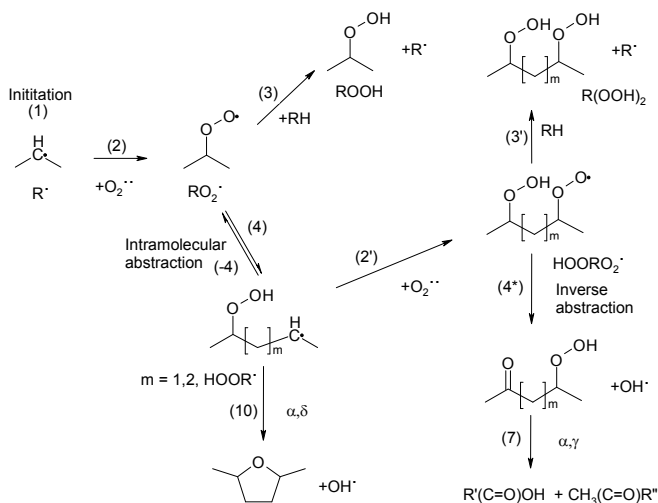


Figure 2. Summary schematic for oxidation of hexadecane at 120-190° C taken from reference [21].

It should be noted that in the investigations just described a plentiful supply of oxygen was provided. Alternative reactions may be more important when the availability of oxygen becomes limited. As an example, such a situation was simulated by heating ethyl-naphthalene in the presence of di-*tert*-butylperoxide in tubes sealed under vacuum. High yields of dimerised product (2,3-dinaphthylbutane, C₂₄H₂₂) were obtained [23]. A scenario whereby hydroperoxides and free radicals form in the presence of oxygen (Figure 1) and later generate more stable, benzylic radicals from alkylated aromatics, leading to coupling of aromatic ring structures, may thus be envisaged.

A conceptually similar scheme, i.e. hydrogen abstraction from cycloalkanes by alkylperoxy and alkoxy radicals has been proposed [24]. Whilst such reactions are typically considered to be important at higher (pyrolysis) temperatures [25] such a process, requiring some previous cyclisation reaction(s), has been invoked to account for the appearance of aromatics-rich deposits arising from oxidative stressing of n-hexadecane at temperatures as low as 160°C [26]. These reactions are summarised in Figure 3.

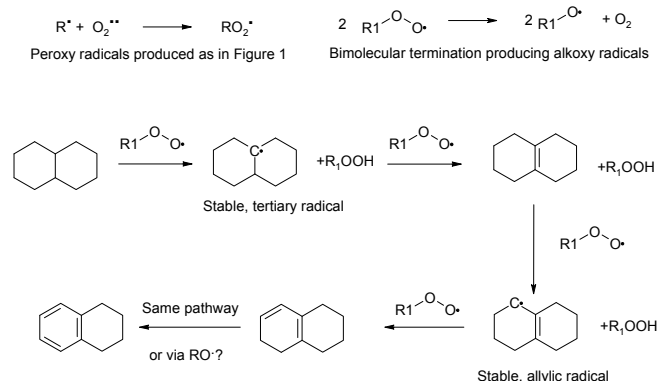


Figure 3. Hydrogen atom abstraction from cycloalkane

AROMATIC CHEMISTRY – Within Figure 1 a generic antioxidant phenol is shown as providing a stable trap for free radicals, interrupting the cycle of oxidation of the aliphatic species and leading to the formation of various, soluble or insoluble, aromatic products. This original proposal [27] has been widely adopted and agreed to explain the apparent inverse relation between the ease of fuel oxidation, in terms of the initial rate thereof, and the amount of deposit eventually formed. ‘Indigenous’ or ‘native’ antioxidants are thereby proposed as a significant source of fuel deposits [28]. Indeed, the difference between a ‘native’ and a synthetic antioxidant may be that only the latter are disposed to yield fuel-soluble products [29].

Highly polar species, extractable from fuels or blending stocks (in particular Light Cycle Oil, LCO) with methanol, have been found to be necessary for the production of insoluble sediment on long-term fuel storage [30]. The methanol extracts were found to comprise polycyclic aromatic materials (phenalenes, fluorenes, phenalenones) and heteroaromatic materials (especially indoles and other N-containing compounds). Detailed analysis of deposits from ambient temperature storage found N-alkyl indoles to be an important constituent [31]. Acid-catalysed coupling reactions of phenalenes, the oxidation product of phenalenes, with indoles have been implicated in deposit formation [32] and shown to provide very similar deposits [33].

It is questionable that diesel deposits produced on long-term storage at ambient temperatures should be identical to those produced from jet or diesel fuels under the conditions of accelerated ageing or recycle through the fuel system. Nevertheless, there exists evidence that they are at least derived from the same set of materials. The concentrations of aromatic and heteroatomic, polar species, both oxygen-containing [34] and nitrogen-based [35], have each been shown to affect the stability of fuel under thermal stress. That the techniques for isolation of these species continue to develop in order to enable the characterization confirms both the importance and the high complexity of the system. This complexity must be seen as reflected in the intractability of the deposits towards characterization.

With this complexity and intractability in mind the following schemes (Figures 4 and 5) are intended to be suggestive of the types of reaction that could conceivably be undertaken by classes of compound and not a definitive account.

The stabilization of phenol- or aromatic amine-derived radicals through the adoption of so-called resonance structures is well documented [36].

The identification of (I) and its oxidation product (II) among the products of 2,6-di-*tert*-butyl-4-methylphenol (Butylated Hydroxy Toluene, BHT) oxidation is evidence that benzylic hydrogen atoms may also be abstracted, see Figure 4 [37].

Oxidation products of BHT (2,6-di-tertiary-butyl-4-methyl phenol)

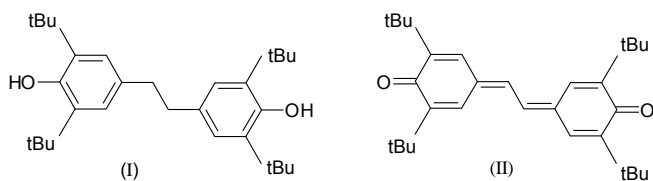


Figure 4. Oxidation products of an antioxidant phenol

Trapping of stable radicals derived from phenols, whether, as shown in Figure 5, by oxygen followed by a bimolecular termination [38] or by involving alkylperoxy radical [39], can lead to formation of quinones.

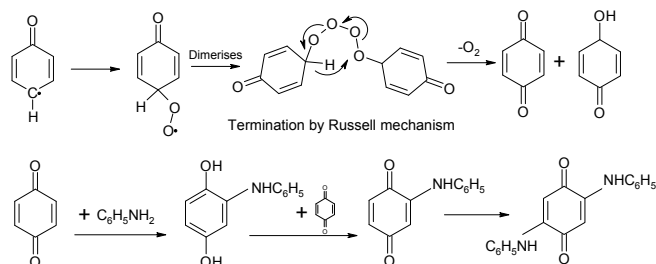


Figure 5. Possible formation and reactions of quinones. Reactant benzene rings are shown as un-substituted for clarity

Quinones are known to undergo redox reactions, form highly-coloured charge-transfer complexes and readily undergo 1,4-additions such as that shown in Figure 5 [40], yielding higher molecular weight O,N-containing products.

DEPOSIT MORPHOLOGY – Deposits are not necessarily physically located at the same point as that at which the chemical reactions leading to their generation occur. Insoluble materials are known to form in the bulk of fuel and the occurrence of surface deposits forming only once fuel has cooled has been reported [41]. The morphology of ‘solid’ deposits arising from hexadecane at 160°C, from diesel fuel at unknown but presumably higher temperatures experienced in injectors [26], jet fuel at 260°C [42] and jet fuel at temperatures in excess of 300°C [43] are strikingly similar. The deposits’ appearance is consistent with their formation as small (<100 nm) liquid spheres in suspension before impaction on the surface before or after agglomeration or aggregation.

A derivatisation study of diesel fuel sediments additionally reviewed the (then) most recent work on the analysis thereof and concluded that all results were consistent with the deposits comprising chemically non-reactive heterocyclic and polycyclic aromatic hydrocarbons physically adsorbed to a core of polar, possibly polymeric material. In the fuels studied, this core was established as containing a large proportion of phenolic hydroxyl groups. Indeed, extent of sediment

formation was positively correlated to the levels of phenolic species in non-hydrotreated LCO [44]. It would seem unlikely that non-hydrotreated LCO could be widely prevalent in recent ULSD. Some sulphur compounds have been found to increase, others to decrease and some to have no effect on oxidative deposition from jet fuel [42]. One report [43] is exceptional in that the deposits are described as aliphatic and containing alcohol, ester, ether and carboxylic acid groups.

These and other ([30]-[34]) apparently disparate results can be unified in a general mechanism as follows:

- It is proposed that all hydrocarbon fuels are capable of providing carbonaceous deposits.
- The inter-fuel variation lies in the intensity and duration of thermal, oxidative and mechanical stresses required to bring this about.
- The initial stages are most likely the formation of hydroperoxides from n-alkanes (or n-alkane-like fragments of other molecules).
- These initial stages may be metal-catalysed or due to exceptionally reactive fuel components.
- Dependent on the levels of the relevant materials in a particular sample, O- and/or N-containing aromatic species act as radical traps, become oxidized and undergo coupling and/or acid/base reactions.
- Molecular weight and polarity of oxidized products increases and/or fuel cools such that a solubility limit is reached and phase separation occurs.

The n-alkanes are suggested as the initial source of hydroperoxide formation on the bases of their relatively high concentration in diesel fuel and their vulnerability to preflame oxidation reactions as evidenced by the low octane number of n-alkanes compared to iso-alkanes and aromatic species [45].

The point remains that fuel composition changes induced by widespread production of ULSD would be anticipated to, if anything, increase the level and duration of stressing required to induce the formation of deposits. Whilst the introduction of comparatively reactive components from bio-sources might be anticipated as prone to increase deposit formation, problems have also been experienced with fuels not containing such streams. Some other contributory factor(s) must be sought. The increase in fuel injection pressures is striking. Additionally, increased pressure provides plausible mechanisms yielding species of increased molecular weight and reduced solubility. The reduced aromatics content of ULSD fuels may be expected to reduce the solubility of high molecular weight and/or polar species therein.

EXPERIMENTAL WORK

FUELS TESTED - Fuel samples for testing were selected on the basis of the sources’ views regarding the

consistency with which the fuels had shown deposition-related problems in High Pressure Fuel Injection (HPFI) equipped engines or vehicles. Care was taken to include a fuel featuring bio-component. A standard reference fuel was included for comparison purposes.

Field Samples (FS) FS1 (reported as not causing HPFI deposit issues) and FS3-4 (reported as doing so) were provided by an engine test facility and FS2 (reported as giving HPFI deposit problems) by an end user. Reference Fuel RF06 was obtained from Petrochem Carless. Once in our hands, the fuels were kept under nitrogen in steel, screw cap containers at outdoor ambient temperature until tested. Field samples 5 and 6 were customer supplied, in plastic sample bottles (HDPE and PET). FS5 was sampled from a bulk storage tank; FS6 was of the same origin but sampled from the fuel tank of an HPFI-equipped vehicle. FS3, 5 and 6 contain approximately 20 wt% Fatty Acid Methyl Esters (FAME). Selected physicochemical properties of FS1-4 and RF06 are provided in Appendix 1.

EXPERIMENTAL METHODS - Fuel oxidative stabilities were determined by Modified Rancimat testing according to DIN EN15751. After the Modified Rancimat test, aliquots of water from the attached bubblers and of the partially oxidized fuel were retained. In the particular cases of FS3 and reference fuel RF06 the effects of the testing were examined by Gas Chromatography Mass Spectrometry (GCMS), using a Shimadzu GCMS-QP2010 Gas Chromatograph Mass Spectrometer. Data from base and tested fuels was compared with gas phase samples of the headspace above the retained water sample. Liquid samples (1 μ l) were injected at 250°C with a 9:2 split into a 30 m x 0.32 mm capillary column with a 0.25 μ m DB5 film thickness. Initial column oven temperature of 50°C was held for 1 minute, ramped at 15°C.min⁻¹ to 285°C and held for 15 minutes. Helium carrier gas was used at a linear velocity of 24.3 cm.s⁻¹. For the headspace samples, the water sample (1 cm³) was placed in a headspace vial (15cm³) and incubated at 100°C during 30 minutes. Samples were injected by an automated system using an HS syringe (2.5 cm³) heated to 100°C. For the mass spectroscopy, ion source and interface temperatures were 200 and 280°C respectively. Solvent cut time was 3 minutes, ionization mode was SEI, detector gain mode was relative at a detector gain of 0 kV and 0 threshold. MS data was acquired from 3.5 to 31.6 minutes in scanning mode, from m/z 50-650 at a scan speed of 1250 and event time 0.5 s.

Polar components were extracted from FS5 and 6 by a procedure based on those set out in reference [35]. The methanol extracts were separated from fuel only after prolonged standing to yield a clean interface and taken to dryness under a steady stream of nitrogen. The resulting liquids were re-dissolved in hexane and once more extracted into methanol as above. Both resulting solutions were subjected to GCMS analysis, carried out as above, without further purification.

RESULTS

OXIDATIVE STABILITY BY EN15751 – The traces of conductivity of the aqueous layer against time are shown in Figure 7. According to this method, FS2, reliably reported as giving HPFI deposit problems, is more stable than either FS1 (reported as not doing so) or the reference fuel. The reference fuel shows evidence of oxidation at shorter time than a reported problem-free fuel (FS1) but then proceeds to oxidize more slowly.

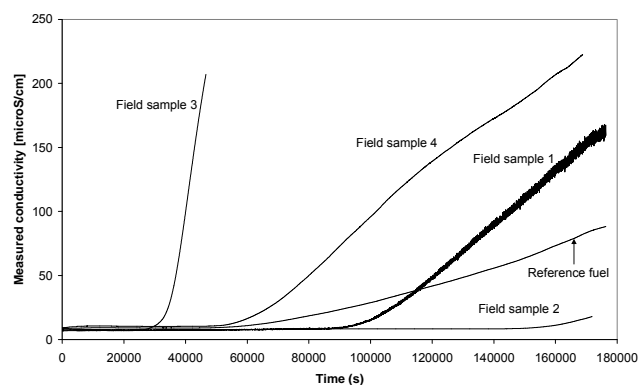


Figure 6. EN15751, conductivity readings from the water trap (μ S.cm⁻¹) versus time (s).

EXAMINATION BY GC/MS – FS3 was chosen for further study as it had shown the most dramatic response. Figures 7, 8 and 9 are the GCMS traces for FS3 as fuel pre- and post-test and of the headspace above the water from the bubbler, respectively. Figure 10 compares GCMS traces for RF06 pre- and post-Modified Rancimat testing.

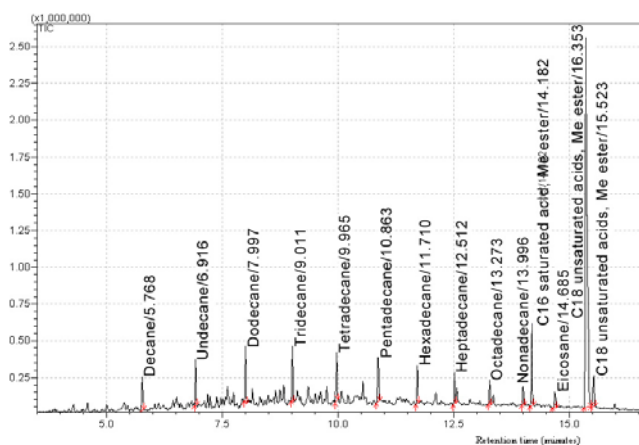


Figure 7. GCMS trace for fuel FS3, pre-Modified Rancimat test.

Figure 7 shows FS3 to comprise a bio-component as revealed by the presence of the methyl esters of C₁₆ and C₁₈ acids at retention times of 14.04 and 15.3 to 15.6 minutes, respectively. Certain of the unsaturated isomers of the C₁₈ acid esters are not well resolved by

this column. This prevented quantification of the extent of any decomposition of the bio-component.

Figure 8 shows the post-test sample to be depleted in lower boiling materials, in particular those of retention time less than about 7.0 minutes. This is ascribed to preferential stripping by the prolonged heating and gas flow. Total ion counts for tetradecane (retention time 10.0 minutes) may be compared to those for the mixed methyl esters of C₁₈ unsaturated acids (15.4 minutes). This semi-quantitative analysis shows the latter to be reducing in concentration much faster than the former (see Table 1). At retention times of around 17.5 minutes a set of peaks identifiable as epoxides derived from the various isomers of C₁₈ acids is now prominent.

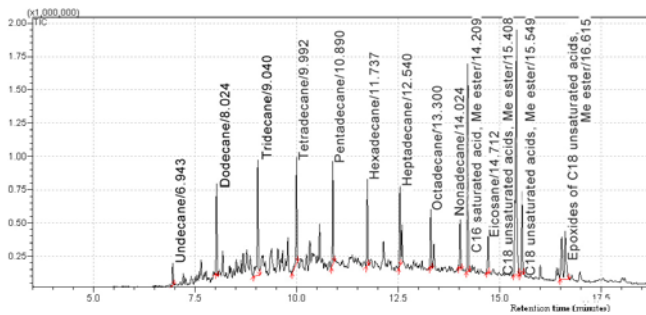


Figure 8. GCMS trace for Field sample 3, post Modified Rancimat testing.

Table 1. Semi-quantitative analysis of GCMS traces for Figures 7 and 8 using tetradecane as internal reference. In C₁₇H_(35-n)CO₂CH₃, n = 2, 4 or 6.

Fig.	Comparison	n-C ₁₄	C ₁₇ H _(35-n) CO ₂ CH ₃
7	Ion count	0.50 x 10 ⁶	6.82 x 10 ⁶
7	Relative	1.0	13.64
8	Ion count	1.35 x 10 ⁶	4.06 x 10 ⁶
8	Relative	1.0	3.01

Figure 9 shows the presence in the water of saturated and unsaturated aldehydes, ketones and alcohols. The presence of these materials is consistent with previous reports for bio-fuels [46] and not unexpected in the light of [19-21] as summarised in Figure 2. It should be noted that the latter references describe studies of a less readily oxidized material under more forcing conditions. Additionally, at retention times between 9 and 11 minutes a number of alkylated aromatic compounds are detected. It is not clear whether these arise from the oxygen-catalysed breakdown of the bio-component or are volatile species present in the fuel, carried over in the air stream and trapped in the water bubbler. That such species have not been reported from earlier studies on bio-diesel, such as [46], would suggest the latter.

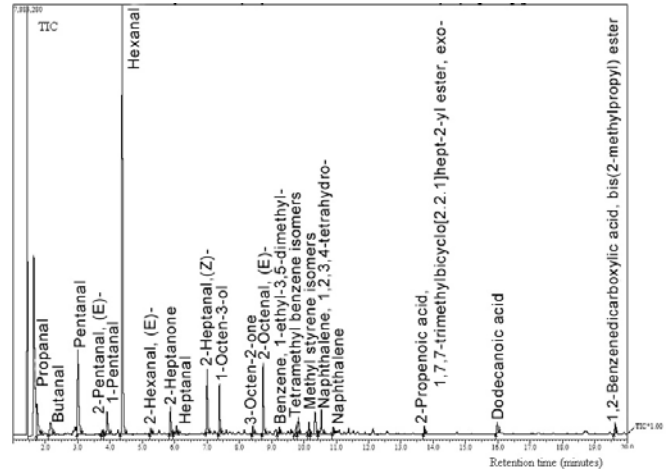


Figure 9. GCMS trace for headspace analysis of water from Modified Rancimat testing of FS3.

Figure 10 illustrates the experimental finding that, beyond the preferential stripping of the light ends (retention times < 8 minutes), no distinction could be made between the pre- and post-test fuels using the GCMS technique, in terms of the identity of the species present. Headspace analysis (not shown) of the water from the bubbler showed no evidence for additional or missing materials.

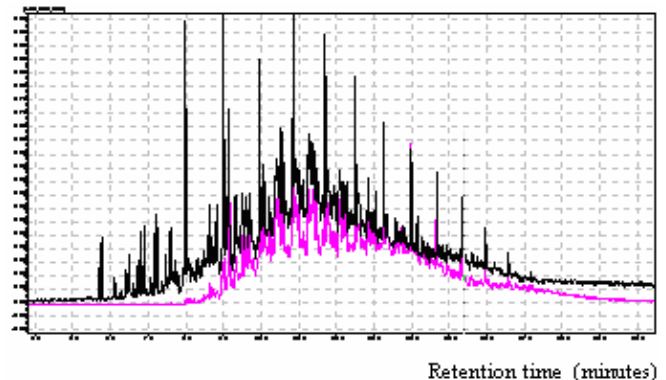


Figure 10. Offset and overlaid GCMS traces for reference fuel RF06 pre- (upper) and post- (lower) Modified Rancimat testing.

FS5 was a light straw coloured, clear fuel containing a small amount of light-coloured solid. FS6 was opaque, having an intense brown colour and contained some black or deep brown solids.

GCMS provided no unambiguous distinctions between FS5 and FS6 (see Appendix 2). Identification of the twenty most prominent species by comparison to the NIST/EPA/NIH Mass Spectral Library (NIST05) did not show any phenolic or nitrogen-containing species. The most prominent species were the C₁₆ and C₁₈ methyl esters, n-alkanes, alkylated benzene, naphthalenes and tetrahydronaphthalenes. The GCMS did not consistently resolve peaks due to unsaturated fatty acid esters. The hexane solutions were richer in n-alkanes, as expected. The full separation method, as set out in reference [35],

includes a high performance liquid chromatography (HPLC) separation. Whilst the solvent extraction provided some resolution, the HPLC step is clearly essential to the collection of tractable data.

DISCUSSION

The EN15751 test method was designed for checking the stability of bio-fuel / mineral diesel blends. Strictly, it should only be applied to fuels containing at least 2% FAME. The reliability of its use on FS1, FS2, FS4 and RF06 can be questioned. It is, however, markedly similar to other standard tests. It features oxidative stress (air bubbled at 10 L.hr⁻¹ through fuel held at 110 °C) and detection of fuel oxidation by a physical method. ASTM D 2274 (95°C, bubbling oxygen at 3 L.min⁻¹, 16 hr) and D 6468 (150°C, vented vial open to air, 3 hrs) employ similar stresses, after which any resulting chemical changes are also detected by physical methods. It was selected for use here largely because the small volume required was better suited to the available sample volumes.

The possibility that other industry standard tests could yet reveal some correlation between physical response to mild thermal and oxidative stress and behaviour in the HPFI engine cannot, of course, be completely discounted. Nevertheless, given the frequency with which such tests are performed and the similarity of the stressing it would be surprising if such a correlation had been overlooked.

A test based on oxidative stress at elevated temperature, i.e. EN15751, has here indicated a given fuel (FS2), reliably reported to give an HPFI deposit issue, to be significantly more stable than both a reference fuel and one reliably reported not to cause problems.

In the case of FS3, a ULSD containing 20 wt% bio-component (B20), the components most vulnerable to oxidation, the unsaturated fatty acid esters, are present at percentage levels. Both the disappearance of the peaks due to the esters and growth of ones due to the resulting products were observed in the GCMS trace. No such readily identifiable markers were present in the case of the reference fuel. At the (low) degree of conversion and/or (high) number of resulting products we were unable to follow the chemistry of the breakdown of the reference fuel by GCMS. In the case of FS5 and 6 a striking difference in appearance of fuel, apparently resulting from circulation through an HPFI system, was not accompanied by any readily-made distinctions in composition.

Our reading of the available literature, as set out in the Introduction, has led us to the following hypothesis. We propose that the stability problems recently observed with ULSD fuels are not due to any previously unseen chemical phenomena, rather, that they arise from increases in the rate or extent to which known processes

occur. A contribution from the decreased ability of fuels to dissolve any such reaction products must also be considered.

Test procedures devised to investigate fuel stability under long term storage using elevated temperature but ambient pressure are unlikely to be informative.

CONCLUSIONS

The possibility that the recent increase in reports of field problems due to deposit formation from ULSD fuels in HFPI engines arises from some new phenomenon cannot, at this stage, be discounted. The impacts of hydrodesulphurization on fuel composition and reactions leading to deposit formation have been considered. The current understanding suggests the following:

- The effects are arising from increases in the rate and /or extent to which the known processes occur,
- That such increases may result from included bio-components and/or increased mechanical stress and
- A contribution from reduction in fuel solvency towards the products resulting from the above.

An industry standard accelerated ageing test has been found not to correlate with a field report of a 'problem' fuel. Other accelerated ageing tests use a similar level of oxidative stress. Attempted chemical characterization of a reported problem fuel has shown that dramatic changes in appearance may be accompanied by at most only subtle changes in composition. Additional test procedures are required in order to study this problem.

ACKNOWLEDGMENTS

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APPENDIX 1

Selected physicochemical properties of test fuels

Property	Density	Cloud point	Cold Filter Plugging Point	Pour Point
Method	IP365	ASTM D5772	IP 309	IP 15
Sample	g.cm ⁻³	°C	°C	°C
FS1	0.8409	-20	-20	-24
FS2	0.8087	-51	-54	-51
FS3	0.8432	-14	-19	-30
FS4	0.8463	-20	-24	-24
RF06	0.8344	-16	-16	-33

APPENDIX 2

GCMS trace for methanol extract of hexane solution of evaporated methanol extracts of fuels FS5 (upper) and FS6 (lower) with vertical scales (total ion count) offset for clarity. Horizontal scale is retention time in minutes.

