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Temperature Programmed Oxidation as a Technique for Understanding Diesel Fuel System Deposits

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ABSTRACT

The fuel injection equipment (FIE) has always been paramount to the performance of the Diesel engine. Increasingly stringent emissions regulations have dictated that the FIE becomes more precise and sophisticated. The latest generation FIE is therefore less tolerant to deposit formation than its less finely engineered predecessors. However, the latest emissions regulations make it increasingly difficult for engine manufacturers to comply without the use of exhaust aftertreatment. This aftertreatment often relies on catalytic processes that can be impaired by non-CHON (carbon, hydrogen, oxygen and nitrogen) components within the fuel. Fuel producers have therefore also been obliged to make major changes to try and ensure that with the latest technology engines and aftertreatment systems the fuel is still fit for purpose. However, there has recently been a significant increase in the incidence of reported problems due to deposit build-up within vehicle fuel systems. Understanding the underlying processes leading to this problem is complicated by the coincident change in vehicle specification to meet the latest emissions limits, the change in fuel sulphur specification and the increasing use of bio-diesel. Various analytical techniques have been used to study these deposits in order to prove or disprove different hypotheses regarding the formation mechanism leading to these deposits.

Temperature programmed oxidation (TPO) is an analytical technique which can be used to determine the oxidation reactivity of the carbonaceous deposits. This may yield additional information regarding the structure of the carbonaceous deposits now being encountered. This paper describes the technique as it has been applied in analysing deposits from vehicle fuel filters and high pressure fuel

injectors. The results from the application of TPO to a variety of the currently encountered deposits is presented and placed within the context of other analytical work used to determine possible causes for this current spate of field problems.

INTRODUCTION

In 1892 when Rudolf Diesel filed a patent entitled “A Process for Producing Motive Work from the Combustion of Fuel” [1] the terms Green House Gas emissions and Global Warming had not entered common usage. However, the claim of Diesel's patent was that by following his process the efficiency of the internal combustion engine could be improved and hence fuel consumption reduced. By adding fuel at a controlled rate to compressed air the rate of heat released could be controlled and therefore the maximum cylinder temperature could be controlled. Diesel claimed that by controlling the maximum cylinder temperature the amount of energy wasted as lost heat would be reduced and the efficiency of the engine increased. As with all good patents the inventor tries to make it as broad as possible and Diesel claimed; “Every kind of fuel in any state of aggregation is suitable for carrying out the process.” However, Diesel's preferred fuel appears to have been “pulverised coal” and Diesel provides an example of his process in which the engine is fuelled with pulverised coal delivered to the combustion chamber via a simple rotating cock mechanism. In reality Diesel never succeeded in making this aspect of his invention into a viable design. The first working prototype of the Diesel engine therefore relied on liquid fuel that was injected with the assistance of compressed air. In 1898 Diesel filed another patent [2] this time claiming a means of controlling the engine by controlling the fuel injected. This design relied on compressed gas to help deliver the fuel which was still specified as being “solid, liquid, gaseous or vapor, or mixtures of these kinds.” In 1900, almost six years

after his first prototype engine had run, Diesel exhibited an engine running on vegetable oil leading to the popular myth that Diesel designed his engine with bio-fuels in mind [3,4,5]. It was thus apparent in the very early development of the Diesel engine that the correct functioning of the fuel injection equipment was paramount to the successful operation of such engines.

In the twenty-first century, with the strict tail-pipe emissions limits imposed by legislation and the customer demand for ever increased efficiency and reduced fuel consumption, the proper functioning of the fuel injection equipment is even more critical to the success of the Diesel engine. After more than a century of development fuel injection equipment is therefore somewhat more sophisticated than that presented in Diesel original patents; this is clearly demonstrated in Figure 1 which shows two examples of modern fuel injection equipment. The left hand side of the figure is taken from a 2009 Denso Corp. patent [6]. Such injectors typically rely on fuel pressure to open the injection valve against a spring pressure, although direct acting injectors are now starting to appear [7].

Where the injection nozzle is opened by the fuel pressure the process is controlled by pressure differences within the injector. These pressure differences determine flows within, in to and out of the injector at a rate determined by the size of critical orifices. The diagram on the right of Figure 1 is taken from a 2009 Yanmar Co. Ltd patent [8], this particular diagram shows some of the critical orifices required to control the rate and quantity of fuel delivered to the combustion chamber.

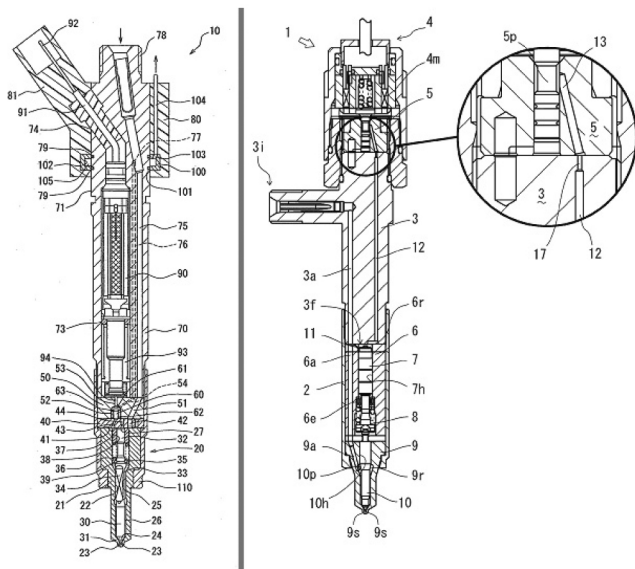


Figure 1. Denso Corp. (left) and Yanmar Co. Ltd (right) injector designs

With such sophisticated injection equipment it is self evident that Diesel's original concept that "Every kind of fuel in any state of aggregation is suitable for carrying out the process" [1] is no longer applicable. The quality of the fuel is now as crucial an element of the total system as the mechanical and electrical hardware. Although a charcoal slurry has been proposed as an alternative fuel for diesel engines [9] it is generally considered desirable to eliminate any solid carbonaceous particles from the fuel reaching the fuel injector. For this reason ever more sophisticated filtration systems [10, 11] are employed to try and ensure that solid particles do not reach the fuel pump or injector.

Due to legislative changes in the US there have recently been step changes in both engine technology and fuel specifications. The introduction of engines to meet the US 2007 emissions certification limits coincided with the introduction of fuel with less than 15 ppm sulphur, a prerequisite to prevent poisoning of the aftertreatment devices [12, 13]. At around the same time the use of fatty acid methyl esters (FAME) or bio-diesel also became more widespread. Coincident with these changes in engines and fuels there was also an apparent increase in the incidence of reported operational problems due to deposit build-up within the fuel injection equipment. However, no matter how sophisticated the filtration systems may be they will only block the passage of material that is in solid form when it reaches the filter. It has been shown that the fuel can undergo chemical change within the fuel injection system leading to the formation of material that is "less fluid" than the system is designed for. This material may be gum and resinous components that form on solid surfaces or it may be solid material that agglomerates within the fuel. Some possible mechanism for the formation of such material has previously been reviewed [14]. However, in order to be certain that the proposed mechanisms are the cause of currently observed deposits it is necessary to fully characterise these deposits.

Many techniques are available and have previously been used to characterise the deposits in fuel injection equipment (FIE) [15, 16]. Many of these techniques are not able to differentiate between the underlying deposit and material that has been adsorbed onto that deposit. For example, most diesel fuels will contain deposit control additives which will be attracted to the deposit. It is therefore only to be expected that the additive will be found on the deposit. This has often led to the erroneous conclusion that the additive is in some way responsible for the deposit.

Many of these analysis techniques also require the deposit to be removed from the FIE component part. Difficulties arise if the deposit is not readily soluble or is in small quantities. Mechanically removing the deposit can also pose a challenge. This paper describes a technique known as temperature programmed oxidation (TPO) and how it has been used to provide additional information of the structure of deposits

within FIE. As used in this work the TPO procedure raises the temperature of the component and in-situ deposit in an oxygen atmosphere and records the evolution of carbon dioxide (CO₂). More amorphous carbon is more reactive than more structured graphitic carbon and therefore oxidises at a lower temperature.

There is an increasing tendency to coat the metal components of FIE to reduce wear [17] or even to reduce the tendency for deposit build up [18]. Various materials have been proposed for wear resistance including oxides [19], metal nitrides [19, 20] and carbides [19]. It is also becoming common to use a Diamond Like Carbon (DLC) coating on fuel injector parts [17, 21, 22]. If the coating contains carbon then this may oxidise during the TPO procedure and the CO₂ evolved from the coating must be taken into account.

EXPERIMENTAL PROCEDURE

EQUIPMENT

The TPO experiments were performed using a Leco® RC612 Carbon/Hydrogen/Moisture Determinator. The device is shown schematically in Figure 2.

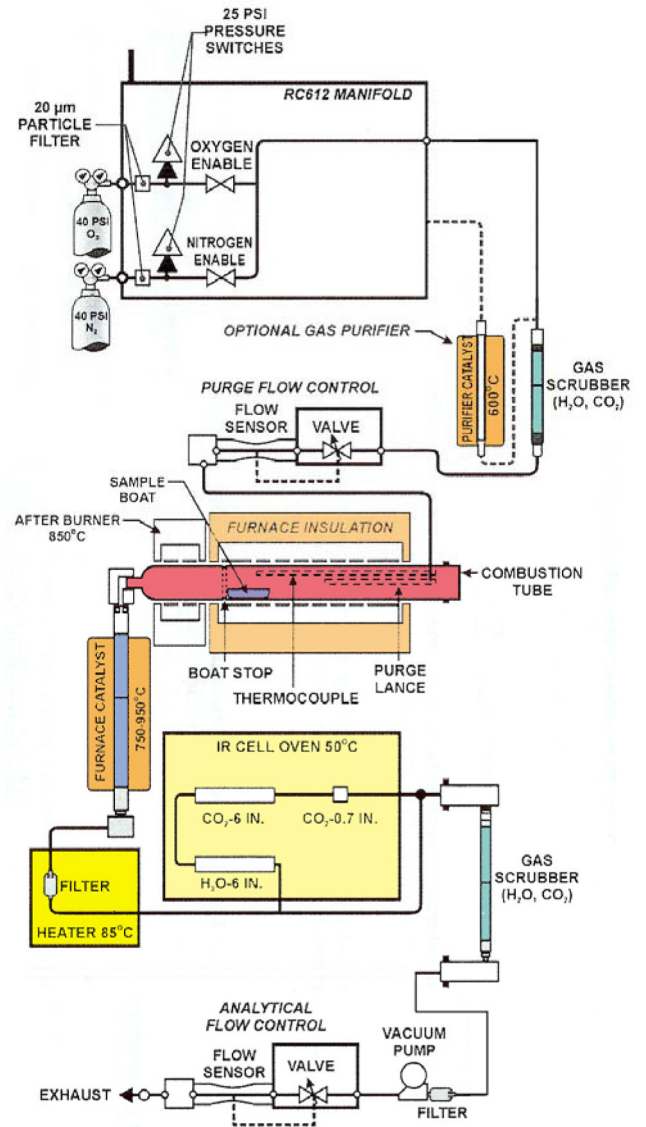


Figure 2. Schematic of TPO system.

The sample was placed in the temperature controlled furnace where it was heated in an oxygen atmosphere. The CO₂ resulting from the oxidation of the carbon is detected by the IR detectors. For the work reported here the starting temperature was 270°C. For initial testing the starting temperature was increased to 1100 °C at a rate of 100 °C per minute. For later testing the final temperature was set at 900°C, again using a ramp rate of 100°C per minute. The oxygen feed rate was 0.75 litres per minute.

REFERENCE MATERIALS

As a reference, a series of commercially available carbon samples were analysed using this method. The samples were sourced from Asbury Carbons and Degussa. A brief description of the samples follows:

Asbury Carbons - AR Binder

Gilsonite, or North American Asphaltum is a naturally occurring resinous hydrocarbon found in the Uintah Basin in the state of Utah, USA and also in Iran. It is similar to a hard petroleum asphalt and is often referred to as natural asphalt, asphaltite, uintaite, or asphaltum. Gilsonite is a shiny, black substance being soluble in aromatic and aliphatic solvents, as well as petroleum asphalt.

Asbury Carbons - GC2

Green coke is a manufactured carbon product resulting from the thermal processing of residual oil, which has been cracked or otherwise processed to remove low boiling fractions. The coke is made by heat-treating the residual oil to a temperature high enough to cause it to polymerise to form a non-melting solid carbon. The coke, as it is removed from the coking process, is referred to as "green coke" and typically contains approximately 15-20% of residual hydrocarbon materials; GC2 typically being at the lower end of this range. Due to its crude oil origins Green Coke can have a relatively high sulphur content. The sulphur content of GC2 is typically about 5%.

Asbury carbons - 4023

Calcined petroleum coke (CPC) is manufactured by heating green coke in a rotary kiln to approximately 1300°C to 1400°C. This removes virtually all residual hydrocarbons and moisture. Again, depending on the petroleum base used to make the coke, the CPC may contain quite high levels of sulphur; 4023 typically contains about 1.5% sulphur. Petroleum cokes are inherently low in ash; 4023 typically containing less than 0.5% ash.

Carbon black (Degussa)

Carbon black is an amorphous carbon solid that is manufactured by the deposition of solid carbon particulates formed in the gas phase. It is generally manufactured by combustion or thermal cracking of a hydrocarbon fuel under reducing conditions. This gives carbon black an inherently low particle size, whereas other forms of carbon usually require milling to achieve the required small particle size. The properties of the various types of carbon black are a function of the "fuel" source used to manufacture the black and the type of combustion process applied.

Asbury carbons - Micro 450

Synthetic graphite is a manufactured product made by high-temperature treatment of amorphous carbon materials. A primary feedstock for the manufacture of synthetic graphite is calcined petroleum coke and coal tar pitch. The manufacturing process consists of various mixing, moulding, and baking operations followed by heat-treating to temperatures between 2500°C and 3000°C. This high temperature is required to drive the solid/solid, amorphous

carbon-to-graphite phase transformation. Because of these high temperatures the impurities contained in the precursor carbons are significantly reduced in concentration. This occurs as a result of the high temperature vaporisation of volatile impurities, which at such high temperatures includes most metal oxides, sulphur, nitrogen, hydrogen, and all organic components that were part of the original petroleum or coal tar pitch. As a result of this thermal treatment, virtually all synthetic graphite products are high purity. Micro 450 is milled synthetic graphite with a nominal particle size of 5µm.

Asbury Carbons - Micro 850

Flake graphite is a naturally occurring form of graphite that is typically found as discrete flakes ranging in size from 50 µm to 800 µm in diameter and 1 µm to 150 µm thick. This form of graphite has a high degree of crystallinity, which equates to near theoretical true density, high thermal and electric conductivity, and low springback. Micro 850 is a natural flake graphite that has been treated to reduce the level of naturally occurring ash constituents to less than 1%. Micro 850 is milled, high carbon flake graphite with a nominal particle size of 5µm.

Asbury Carbons - 146

Grade-146 is milled, natural flake graphite that has a nominal purity of 95%. This graphite material is processed directly from graphite flakes that have not been subjected to any post-floatation purification processes. Grade-146 has a nominal particle size of 20µm.

Asbury carbon has had XRD undertaken externally on its products to establish degree of crystallinity, i.e. amorphous or graphitic. Further, this characteristic may be inferred from the knowledge of the original material source, and simple tests for example density, electrical resistivity, compression density, expansion and even "feel".

For the work reported here the samples were analysed for carbon, hydrogen and nitrogen using a ThermoQuest Flash EA 1112 series CHN-O Analyzer. The analyser operates according to the dynamic flash combustion of the sample. The sample is weighed in a tin capsule and introduced into the combustion reactor via an autosampler together with the required amount of oxygen. After combustion, the reaction gas products are carried by a helium flow to a layer filled with copper, then through a GC column that provides the separation of the combustion gases and finally detected by a Thermal Conductivity Detector. Total run time is less than 8 minutes and a complete CHN report is automatically generated by dedicated software and displayed at the end of the analytical cycle. The results of this analysis, expressed as percentage mass, are shown in [Table 1](#).

Table 1. Reference carbon sample C/H/N analysis

Standard	Analysis (in-house)		
	C	H	N
Asbury Carbons - AR Binder	84.86	10.14	3.23
Asbury Carbons - GC2	85.94	2.84	2.53
Asbury carbons - 4023	95.69	0.07	1.26
Carbon black	81.27	0.89	0.57
Asbury carbons - Micro 450	98.04	0.005	0
Asbury Carbons - Micro 850	98.10	0.01	0
Asbury Carbons - 146	88.61	0.02	0

The results of the TPO analysis on these commercial carbon samples are presented in Figure 3. The CO₂ emissions were normalised so that the peak emission value is unity.

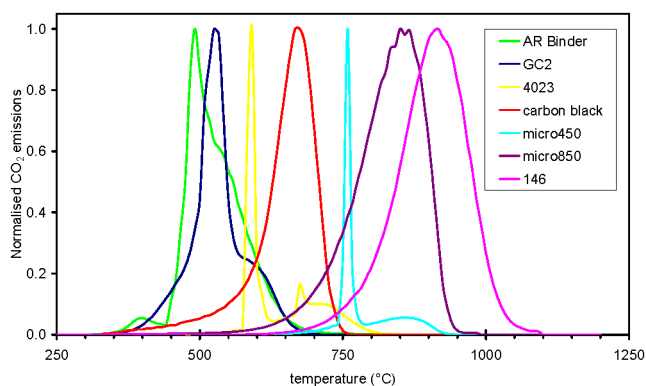


Figure 3. Normalised CO₂ emissions for reference carbons

From these tests the temperature of the peak CO₂ emissions was determined. Three repeats of each reference carbon sample were performed to give an indication of repeatability. Table 2 shows the temperature of the peak CO₂ emissions. Whilst it is recognised that three repeat tests do not meet the usual statistical requirements, the coefficient of variance (CV) was nevertheless calculated and is included in Table 2. It is clear from Table 2 that the graphitic carbons, the last three rows in the tables, exhibit a far higher temperature of peak CO₂ emission, i.e. they are more thermally stable than their amorphous counterparts.

(See Table 2 after last section of paper)

Figure 4 has been plotted to show the peak CO₂ emission temperatures, with error bars indicating plus and minus one standard deviation, against the percentage carbon in the reference carbon samples. The reference carbon samples have been divided into amorphous carbon and graphitic carbon. From Figure 4 it is clear that there is only a very loose correlation between the carbon content of the reference carbon samples and the temperature at which they oxidize but that there is a distinct difference between the thermal stability of the carbon according to its underlying structure. The TPO therefore provides additional insight to that obtained from C/H/N analysis.

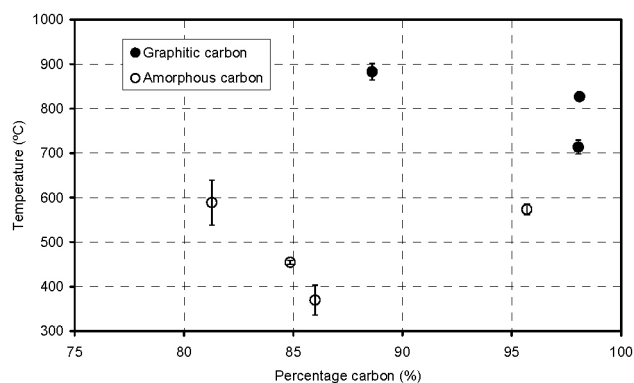


Figure 4. Peak CO₂ emission temperature against percentage carbon in sample

Metal oxides are known to reduce the temperature and increase the rate at which oxidation of carbon will occur [23, 24]. Work with fuel borne catalysts to aid diesel particulate filter (DPF) regeneration has shown that the hydrocarbon content of diesel soot can also have a significant effect on the oxidation process [25]. Work was not performed during this study to quantify any possible catalytic effects although it is worth noting that the sample with the highest ash content was Asbury Carbons - 146, which typically contains about 3.5% ash, produced a CO₂ emissions peak at the highest temperature.

FIELD SAMPLES

PREPARATION OF FILTER DEPOSIT SAMPLES.

Fuel filters were collected from a variety of geographic locations, as well as equipment type. These filters had been replaced before the normal replacement interval due to operator complaints of loss of power and/or excessive noise and vibration. The used fuel filters were obviously “fuel wet” and the following procedure was followed to enable the separation and characterization of both the soluble and insoluble moieties. A section of the filter element (15cm by 3cm) was cut from the filter and weighed to enable the determination of residue levels. The filter section was then

subject to various analytical techniques which have been previously reported [15]. The deposit was extracted with HPLC (High Pressure Liquid Chromatography) grade tetrahydrofuran (120mL), either by 15 minutes in an ultrasonic bath, or an overnight soak. The liquor was filtered off and the remaining solid was washed in pentane to remove any remaining diesel fuel. This solid material was then analysed as described in [15, 16] and by TPO.

PREPARATION OF FUEL INJECTOR DEPOSITS.

The deposits found on fuel injectors are typically of limited volume making it difficult to remove a sufficient quantity of deposit to carry out comprehensive analysis. As noted above, TPO thus provides a significant advantage over other techniques where there is a limited sample volume. The fuel injectors were mechanically disassembled. To remove any residual diesel fuel the individual injector parts were then washed in toluene followed by washing in acetone. The injector components were then dried in an oven at 65°C.

RESULTS

A number of fuel injectors and fuel filters were collected from the field having been removed from vehicles showing problems. In all cases the operators had complained of a significant loss of power from the vehicle. The fuel injectors were subject to scanning electron microscopy (SEM) and TPO analysis.

FILTER DEPOSITS

Previously reported work [15, 16] had investigated the composition of the deposits found in the fuel filters of vehicles equipped with engines utilising high pressure common rail systems. The conclusions drawn were that the filters not only contained the expected fuel residues, water and metallic swarf; they also contained carbonaceous material which has been shown to contain elemental carbon, straight-chain and substituted alkanes, cycloalkanes, aromatics, polyaromatics, acids, and inorganics. The quantity of these various constituents was influenced by the vehicle/engine type and duty cycle. To investigate the nature of these deposits further, other techniques have been employed and are reported here. These additional techniques were Transmission Electron Microscopy (TEM), x-ray diffraction (XRD), Thermogravimetric analysis (TGA) and TPO. The latter proving to be a useful tool in describing the carbon types in the deposit. The TPO technique is also useful when the sample size is limited as was the case with some of the filter samples or where in-situ analysis of a deposit is required such as for the fuel injector.

Transmission Electron microscopy

The TEM data shows the deposit to be mainly an amorphous char; this is shown in Figure 5. However, closer inspection of areas of the deposit shows some carbon structure; this is shown in Figure 6. However, this carbon structure was not as crystalline as has been seen in earlier work on jet fuel [26].

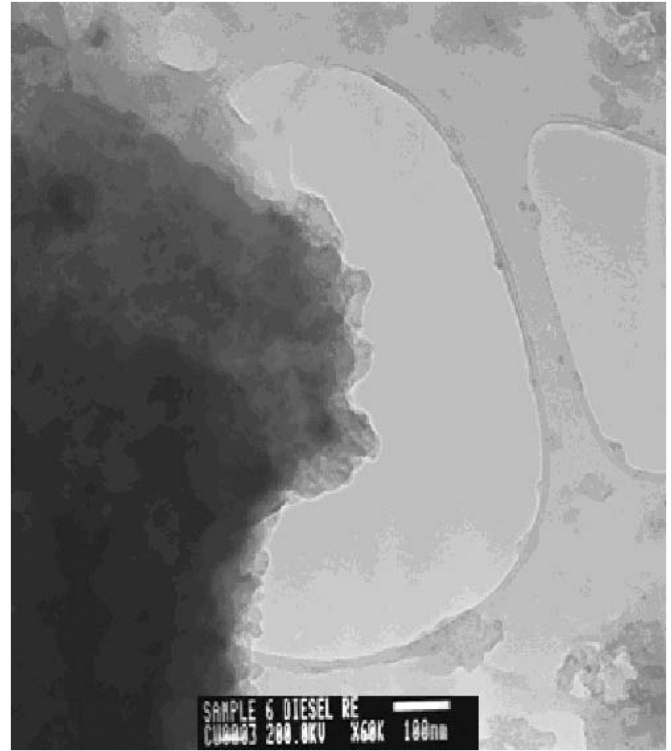


Figure 5. TEM at x60k (100nm) of sample from field filter

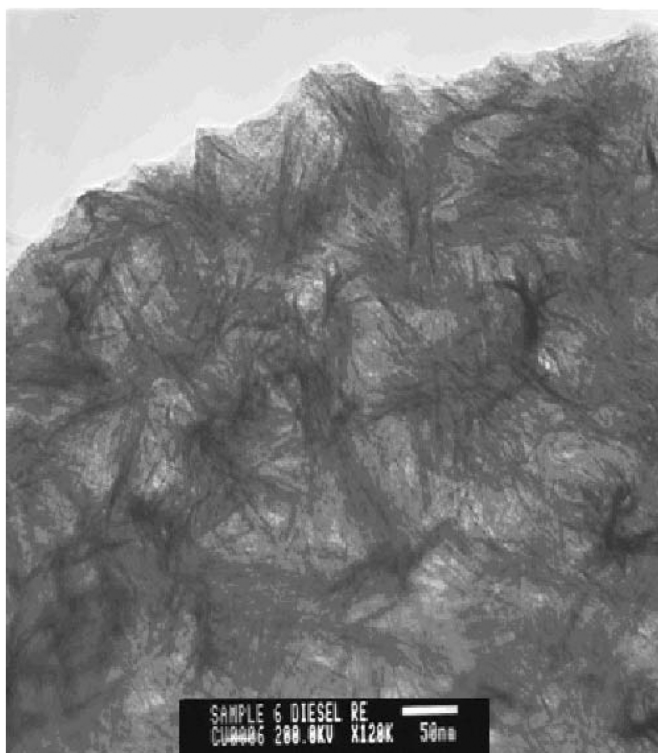


Figure 6. TEM at x120k (50 nm) of sample from field filter

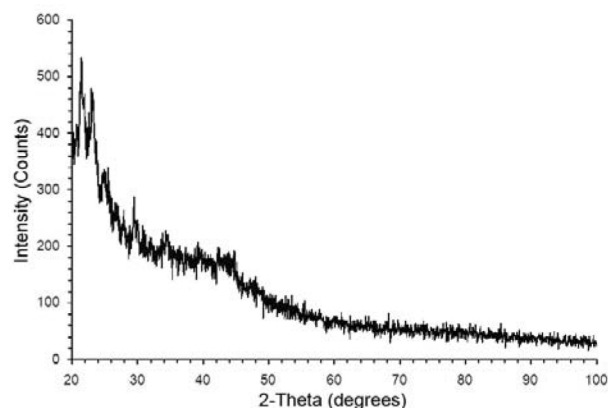


Figure 7. XRD pattern of the diesel residue.

A quantitative estimate of the carbon present in the deposits where sufficient sample was available can be made using TGA. The application of TGA in fossil fuel research dates back many years [29,30,31], with the technique being used to differentiate between volatile matter and elemental carbon. The method involves determination of the volatiles under nitrogen to 1000°C and then the carbon burn off of that residue in air to 1000°C to yield the carbon and inorganics present. For the work reported here, a TA Q500 TGA was used and the sample was heated under nitrogen at a flow rate of 60 mL/min. The sample was heated from ambient to 1000°C at a rate of 20°C/min. The sample was then allowed to cool to ambient and the procedure repeated under air. The results of the TGA for four filter samples are presented in [Table 3](#).

X-Ray Diffraction

It is known that crystalline carbon produces signals at 26° and 72° [27, 28]. [Figure 7](#) shows the XRD pattern produced by the diesel fuel filter residue. This figure shows that these peaks are not present and that the carbon in the filter residue samples is mostly amorphous. The conclusion is that the deposits are mainly amorphous with some carbon present which has structure. This would be expected from the filter which would collect a number of carbonaceous deposit precursors, carbon deposits and a mixture of fuel-borne impurities.

Table 3. TGA results for four filter samples

Sample	Volatiles (% mass)	Carbon (% mass)	Inorganics (% mass)
A	65.2	15.4	19.4
B	74.7	16.9	8.4
C	84.3	1.7	14.0
D	88.3	1.3	10.4

These results illustrate the variability in the composition of the deposits, which is clearly a result of differing vehicle duty cycles and/or fuels.

Results of the TPO analysis are shown graphically in [Figure 8](#) and the results of the H/C analysis and the peak CO₂ emission temperatures from the TPO are also tabulated in [Table 4](#).

Table 4. Comparison of H/C ratio and Peak CO₂ emission temperatures for four filter samples.

Sample	Atomic H/C ratio	Peak CO ₂ emission temperature (°C)
FDS 01	1.72	457
FDS 02	1.34	352
FDS 03	1.66	296
FDS 04	1.45	367

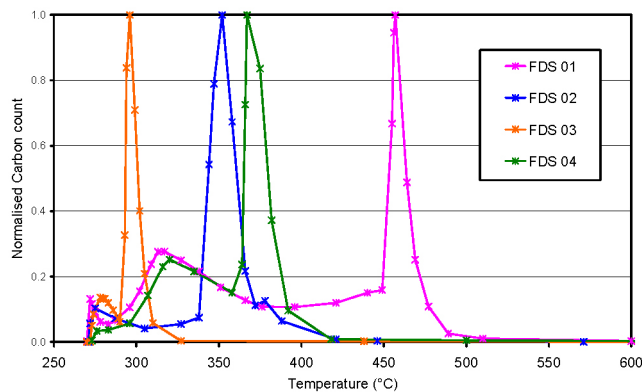


Figure 8. TPO results for filter deposits

In Figure 8 the higher temperatures to the right of the chart indicate that a higher degree of ordering of the carbon atoms is present, i.e. it is more graphitic in structure. However, as was suggested in Figure 4; there is not necessarily a correlation between the H/C ratio and the degree of crystallinity in the carbon structure and hence the peak CO₂ emission temperature. This is demonstrated by the results shown in Table 4; for example, samples FDS 01 and FDS 03 are the two samples having the closest H/C ratio. However, they are in fact the most diverse regarding the degree of order in their carbon structure. Thus, the TPO analysis has shown deposits with a different degree of carbon crystallinity are formed during the degradation process. Although H/C analysis shows the deposits to be more characteristic of fuel rather than graphite, there are variations in the degree of carbon crystallinity present in these deposits.

If sufficient sample volume is available then the TPO technique allows a larger sample to be analysed than does the TGA, this reduces the risk of the small TGA sample being non-representative of the bulk sample. However, if the sample volume is small or it must be analysed in-situ then the TPO technique is still applicable. This is demonstrated with fuel injector deposits which will be discussed below.

INJECTOR DEPOSITS

The injectors obtained from the field had different amounts of visible deposit. These deposits were not soluble in standard solvents. Physical removal of the deposits was difficult as the physical removal process may remove material from the injector part itself or from the “scraper” used to remove the material. Such “foreign” matter would then produce erroneous results from subsequent analysis. In many cases, the amount of deposit was also very small. It was thus considered that TPO would be an ideal analysis technique for these deposits as the injector parts could be analysed with the deposit in-situ. The findings from these analyses are presented below.

Carbon containing coatings

As noted in the introduction, many modern fuel injectors have a coating on some of their component parts. In many cases this coating contains carbon, for example, DLC coatings. This must therefore be considered when analysing the results of the TPO.

Figure 9 shows the normalised TPO traces from four different fuel injector needles. Two of the traces (IDS-01 and IDS-02) are from injectors collected from the field. Also included in the figure is the trace for a new injector for the Peugeot DW10 engine as used for deposit forming tendency testing [32] and a trace for a used DW10 injector.

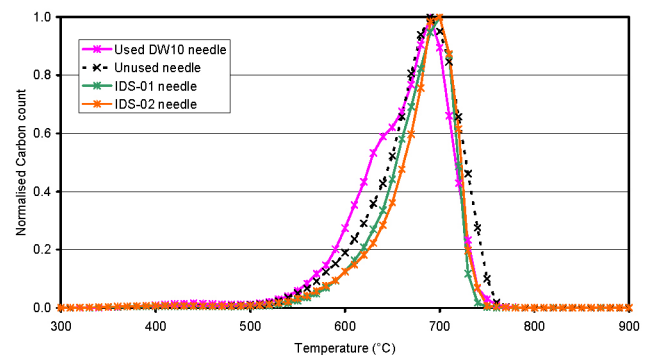


Figure 9. Normalised TPO traces showing the presence of DLC type coating

As can be seen from Figure 9, the peak carbon emission occurs at a temperature of between 690°C and 700°C. The two injectors taken from the field had very little visible deposit on their needles. The used DW10 injector showed a slight lacquering of the needle.

Considering that the traces for IDS-01 and IDS-02 closely match that of the unused injector needle it is assumed that these traces show negligible deposit but only the presence of the coating. These two traces were taken as further indication of the good repeatability of the test method. The “hump” in the trace for the used DW10 injector is indicative of the

lacquer seen on the needle. By subtracting the normalised trace for the un-used injector from that of the used injector gives an indication of the trace that would have been produced had the needle coating not been present. This gave a peak carbon emission at a temperature of 630 °C. This is slightly above the temperature of the peak emission observed for the amorphous carbons used as a reference and shown in [Figure 4](#).

Field Injectors

A number of injectors were sourced from the field, having been replaced as the vehicles were reported to have had problems. These injectors were stripped and subjected to SEM analysis and TPO. As an example, one of the injector needles is shown in [Figure 10](#). General and spot analysis of the needle revealed the presence of the same elements, namely Cr, Ag, Fe and traces of Ca and S. The metals Cr, Ag and Fe are believed to be from the needle itself, the S will be present in the fuel. The source of the Ca is not known, it is thought unlikely that this could be lubricant derived as there was no Zn or P detected. It is also worth noting that there was no Na or K detected. This is taken as evidence that the engine had not been run on bio-diesel or that if bio-diesel had been used it did not contain Na or K. The metals commonly associated with catalytic degradation of fuel and other deposit forming reactions were not apparent.

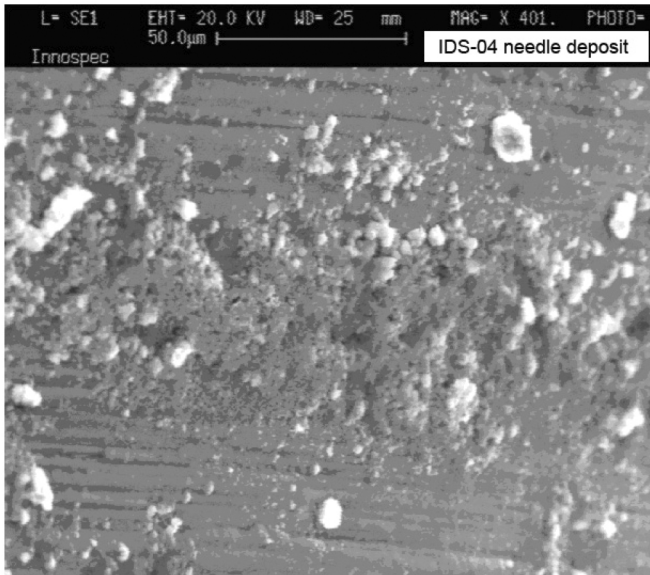


Figure 10. SEM of deposits on needle IDS-04

The nozzle tip from the same injector was also subjected to SEM and an image of one of the holes is shown in [Figure 11](#).

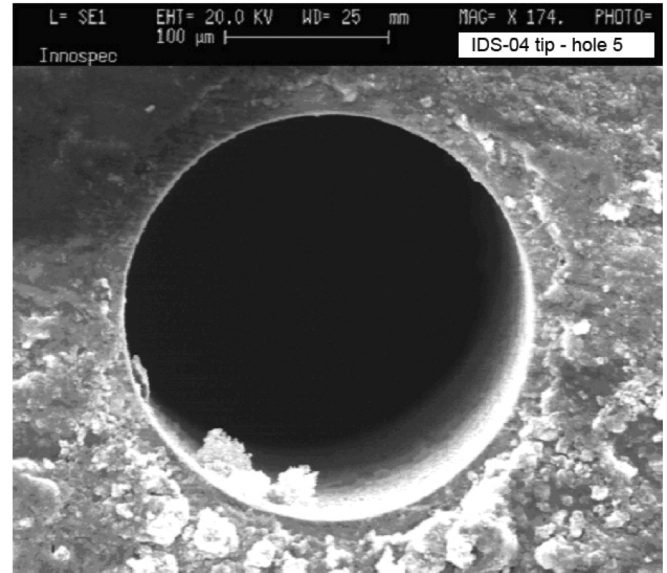


Figure 11. SEM of deposits on nozzle tip of IDS-04

As can be seen from [Figure 11](#) there is deposit build-up around the nozzle hole but generally the hole is free of significant quantities of deposit. The small amounts of granular deposit seen towards the bottom of the hole in this image, about the 7 o'clock position, are thought to have been transported there during the handling of the injector, including removal, packaging, transportation, etc. This type and quantity of deposit is likely to be removed during any subsequent high pressure injection event. It is therefore unlikely that deposits within the hole of this injector were the source of operational problems.

Some of the injectors however had far more significant levels of deposit within the nozzle holes. This is illustrated in [Figure 12](#).

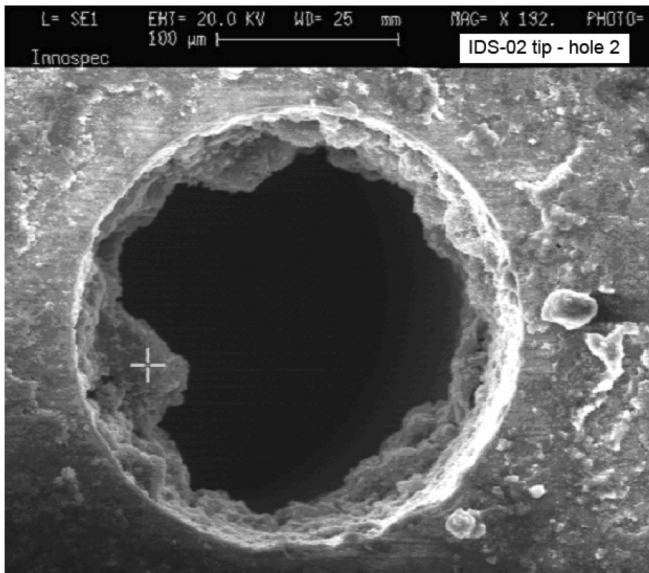


Figure 12. SEM of deposits on needle IDS-02

As can be seen from [Figure 12](#) the deposit build-up is present all around the circumference of the hole and appears to be present well into the depth of the hole. Analysis of [Figure 12](#) also indicates that the thickness of this layer of deposit is approximately 5% of the diameter of the hole, i.e. it reduces the diameter of the hole by approximately 10%. A 10% reduction in hole diameter would lead to a 19% reduction in flow area. This is likely to produce a significant loss of power.

It is not currently known whether these deposits are formed within the nozzle hole or whether they are transported there from the combustion chamber during the expansion stroke when the combustion chamber pressure forces combustion gases into the nozzle holes.

If a method can be developed for removing the deposits from the outer surface of the injector tip without disturbing the deposits within the holes then TPO can be applied to determine the nature of the deposits within the holes. If sufficient deposit has been removed from the outer surface then this could also be analysed by TPO. Alternatively a subtraction process could be used as has been demonstrated with the carbon coating on the injector needles. This would be an interesting topic for further research as it would add valuable information regarding the mechanisms of deposit formation within the injector holes.

[Figure 13](#) shows the TPO results for two similar fuel injector tips along with the trace for the unused DW10 injector with the DLC type coating. The results have been normalized such that the peak CO₂ emission equals unity.

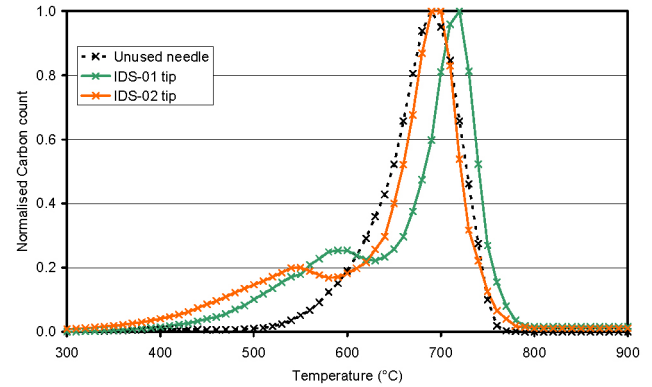


Figure 13. Normalised TPO traces for injector tips and unused needle with coating

It can be seen from this chart that the major CO₂ emission occurs in the same temperature region as the DLC like coating. It is therefore assumed that this emission is from a coating within the injector tip. The secondary shoulder peak for both injectors is thought to be caused by the small amount of deposit on the outside of the injector tip.

In both cases, this deposit material has a peak emission in the range of 550°C to 600°C. Reference to [Table 2](#) and [Figure 4](#) suggests that this is in the same temperature range as carbon black and below the temperature at which graphitic carbons burn. This is as expected, as it is assumed that the majority of deposits on the outside of the injector tip are derived from the products of combustion within the combustion chamber.

[Figure 14](#) shows the TPO results for both the nozzle tip and the needle for an injector sourced from the field. Again the results have been normalised such that the peak CO₂ emission equals unity. From this figure it is clear that the nature of the deposits on the injector tip are significantly different in nature to those found on the needle. For the nozzle tip, the peak emission temperature is between 530°C and 540°C. This is just below the values observed for the two nozzle tips presented in [Figure 13](#) but is again indicative of carbon black. The peak CO₂ emissions from the needle deposits occurred at about 650°C. This temperature is higher than any of the amorphous carbons tested as a reference but equally it is below any of the graphitic materials tested as references.

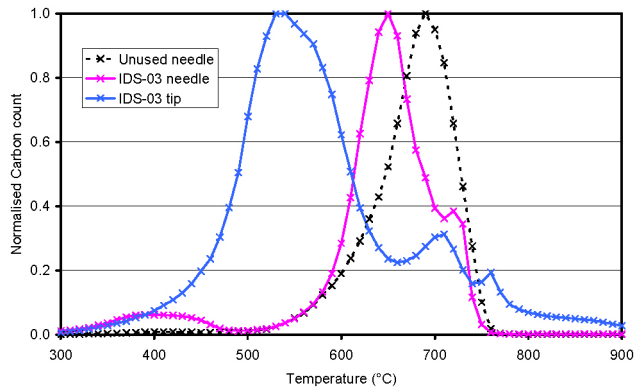


Figure 14. Normalised TPO traces for field injector tip and needle plus unused needle with coating

Each of the field sample traces shown in [Figure 14](#) has additional peaks at higher temperatures in the same region as the DLC like coating. The data has been re-normalised so that the peak in the region of 690°C to 720°C has a value of unity. This data is presented in [Figure 15](#).

It is clear from [Figure 15](#) that these additional peaks are very close to that for the DLC type coating of the DW10 injector; the unused needle has a main peak at 690°C and a second peak at 720°C and the tip has a main peak between 530°C and 540°C with a second peak at 710°C. These values are also consistent with the values for the nozzle tips shown in [Figure 13](#). Both the needle and the nozzle tip also show third peaks; for the needle this is a small “hump” peaking at around 390°C and for the nozzle tip a more pronounced peak at 760°C. This temperature is close to that at which the graphitic reference samples were producing peak emissions.

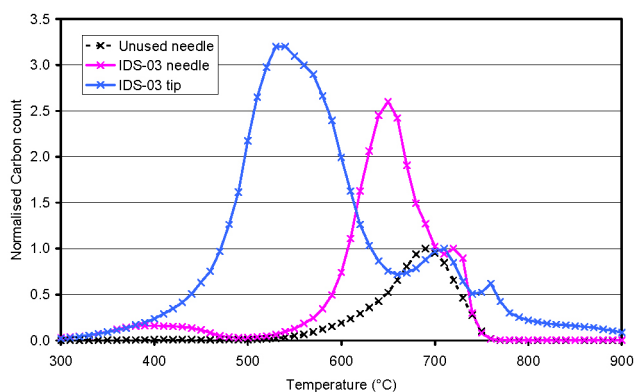


Figure 15. TPO traces for field injector tip and needle plus unused needle with coating, normalised to coating peak.

DISCUSSION

Analysis of reference samples of carbonaceous material showed only a loose correlation between the H/C ratio and

the temperature at which the TPO indicated the maximum rate of oxidation. Amorphous carbon materials produced peak oxidation rates at noticeably lower temperatures than the graphitic type reference materials. Analysis of samples taken from fouled fuel filters obtained from the field showed a similar lack of correlation between the H/C ratios and the temperature of peak CO₂ emissions produced in the TPO experiments. The TPO analysis indicated that the material trapped in the fuel filters tended to be of amorphous type carbon, although in some cases, there was indication of very small amounts of material with a more crystalline carbon structure. This provides a degree of agreement with what has been postulated from TEM analysis.

TPO analysis of an unused common rail fuel injector showed clear evidence of a carbon containing coating on certain component parts. TPO analysis of a used example of the same type of injector showed a peak rate of CO₂ emissions at the same temperature although the rate of emissions at higher temperatures was noticeably lower. It is not yet known whether this is due to test to test repeatability, injector to injector repeatability or whether there is a slight change in the morphology of the coating as a result of injector use. Further work is required to answer this question. TPO analysis of two used injector needles, taken from the field, showed the presence of a carbon coating but insignificant deposit. There was very good agreement between these two samples suggesting test repeatability is good. The temperature at which the peak oxidation rate occurred for the coatings on these injector parts was lower than the graphitic reference carbon samples suggesting that there was less structure to the arrangement of the carbon atoms in the coatings than in graphite.

The TPO analysis of injector parts taken from replaced field injectors showed that the nature of the deposits was significantly different from those found in the fuel filters. This indicates that there are not significant quantities of deposits being formed within the fuel injectors that are then being transported back to the fuel tank only to be subsequently picked up and trapped in the fuel filter. It is still possible, and from previous work [14] thought highly likely, that deposit precursor are formed within the high pressure regions of the fuel injection system but the ultimate fate of these precursors depends on whether they are returned to the fuel tank or are carried through to the fuel injector.

The characteristics of the deposits formed on the fuel injector needles are significantly different from that formed on the tip of the injector. The deposits found on the tip of the injector appear to be more amorphous in nature than those on the needle. A previous study [33] using TPO and Raman Spectroscopy to compare soot formed by a spark discharge generator and diesel soot from a EuroIV engine showed the CO₂ emissions from the diesel soot beginning at about 150°C

and continuing to rise to 500°C. Unfortunately their work stopped at this temperature but although the start of CO₂ emissions is at a somewhat lower temperature than that observed for the tip shown in [Figure 15](#); the sharp rise in CO₂ emissions between 400°C and 500°C is similar to that observed in [Figure 15](#). In contrast the CO₂ emissions from the injector needle deposits do not start to rise until almost 500° peaking at 650°C. Later work by the same group [34] showed no significant difference in the morphology of soot taken from a Euro IV and a Euro VI engine. This would suggest that the deposit on the injector tip is derived from combustion residues. With the introduction of bio-diesel to the blending pool much work has recently taken place to investigate whether the addition of bio-diesel significantly alters the structure of the soot produced [35]; with particular emphasis on the effect this might have on aftertreatment performance [36]. Collection and analysis of combustion chamber deposits and exhaust soot samples would prove an interesting comparison to injector tip deposits. More work is required to develop a technique to allow differentiation (if any exists) between the small amounts of deposit formed within the injector holes and that formed outside of the holes. The injectors from the field were of the sac type, the DW10 injector is of the valve covered orifice (VCO) type, and the amount of fuel left on the combustion chamber side of the injector needle seat may have an influence on the deposit formation mechanism in this area. The deposits formed on the injector needles tends to burn-off at higher temperatures suggesting that it contains more structured carbon, i.e. the deposits are more graphitic in nature.

CONCLUSIONS

Temperature programmed oxidation (TPO) was investigated as a technique for gaining additional information regarding the structure of deposits in high pressure fuel injection systems. This was part of an on-going programme of work to determine the nature and probable causes of these deposits. The TPO technique highlights the oxidation reactivity of the carbonaceous material; this provides some indication as to the degree of crystallinity of the underlying carbon structure. Carbon that is more amorphous is more reactive than more structured graphitic carbon and therefore oxidises at a lower temperature.

The TPO technique allowed for the in-situ analysis of deposits on injector parts. This was a significant advantage where levels of deposits were extremely small and/or difficult to remove. The technique also proved valuable in ensuring an averaged result was obtained when a larger sample was available where other techniques such as TGA may have required multiple measurements to allow for possible sample inhomogeneity.

Comparison of the H/C ratio and the TPO analysis of both reference carbon samples and samples of deposit taken from

used fuel filters showed poor correlation. The H/C ratio cannot therefore be taken as an indication of the crystallinity of the carbon structure. The TPO analysis therefore provides additional useful information.

The TPO analysis carried out on injector parts clearly showed the presence of a carbon containing coating on many of the injectors that were studied. Using the TPO data from an unused injector of the same type allowed for the subtraction of the CO₂ emissions from the oxidation of the coating to provide information regarding the deposit. The technique appears repeatable although additional work is required to explain differences between the measurements from a used and an unused example of the same type of injector.

The deposits formed on the injector tip were found to be more amorphous in nature whilst the deposits formed on injector needles were more structured. This is in keeping with the injector tip deposits being derived from combustion products. Some of the deposits formed on the injector needles exhibited a degree of oxidation reactivity close to that of the carbon based coatings although they were still more reactive than reference samples of graphitic carbon. This suggests that these deposits are formed within the fuel system by a totally different process.

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Table 2. Peak CO₂ emission temperatures and CV for the reference carbon samples

Standard	Temperature of peak emissions (°C)	CV (%)
Asbury Carbons - AR Binder	455	1.0
Asbury Carbons - GC2	370	9.1
Asbury carbons - 4023	574	2.1
Carbon black	589	8.6
Asbury carbons - Micro 450	714	2.2
Asbury Carbons - Micro 850	827	0.8
Asbury Carbons - 146	883	2.1