

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

2010-01-1475

Published
05/05/2010J Barker, P Richards, D Pinch and B Cheeseman
Innospec

Copyright © 2010 SAE International

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

**Documents**

Document Sharing Hub

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.

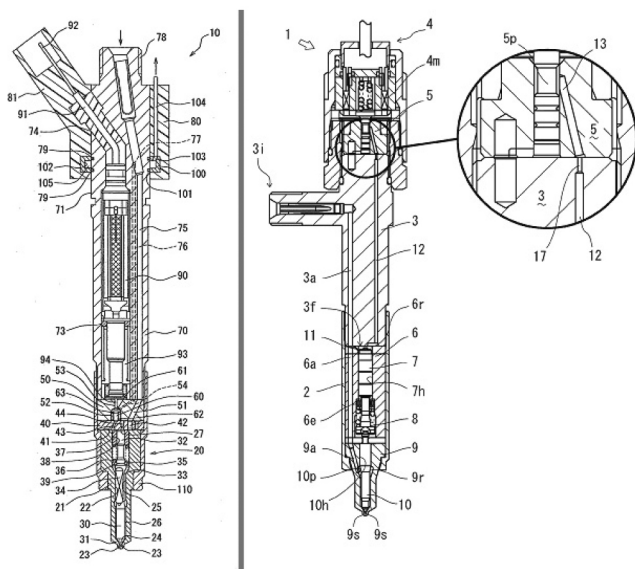


Figure 1. Denso Corp. (left) and Yanmar Co. Ltd (right) injector designs

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 (CO_2). 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 CO_2 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.

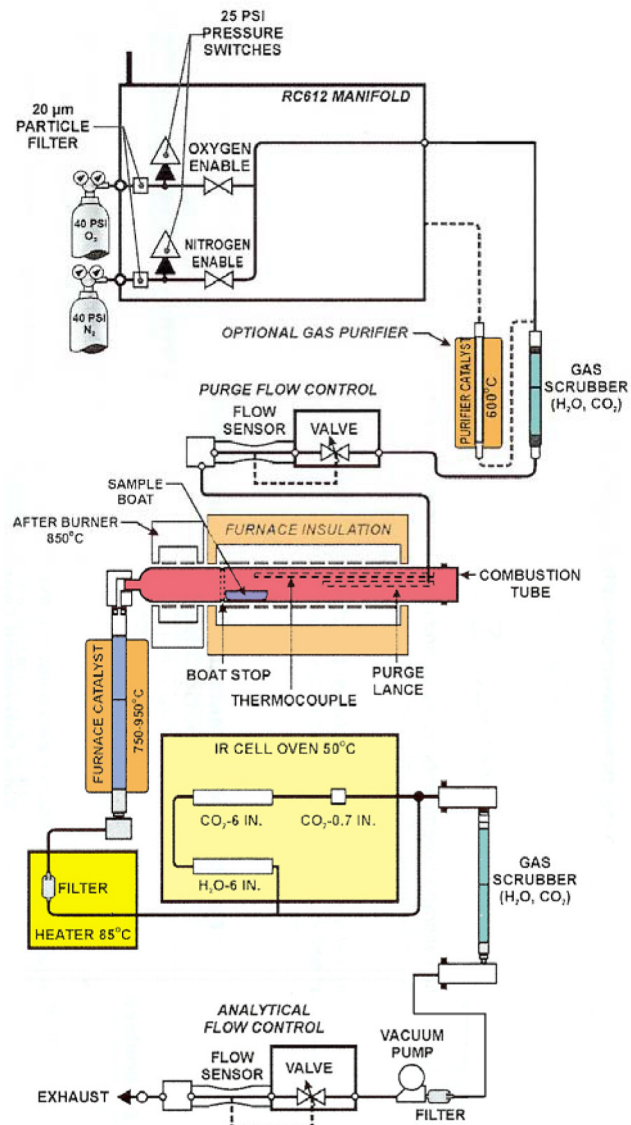


Figure 2. Schematic of TPO system.

The sample was placed in the temperature controlled furnace where it was heated in an oxygen atmosphere. The CO_2 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.

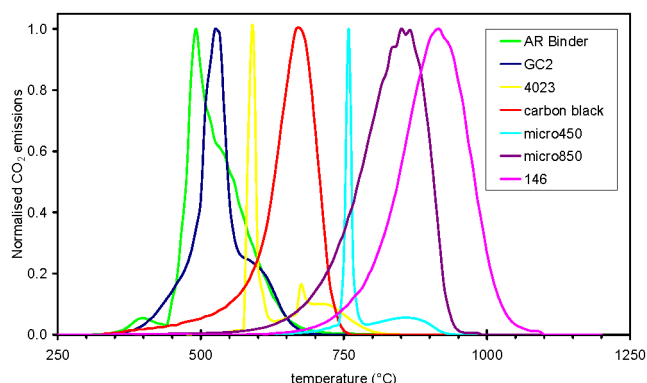


Figure 3. Normalised CO₂ emissions for reference carbons

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.

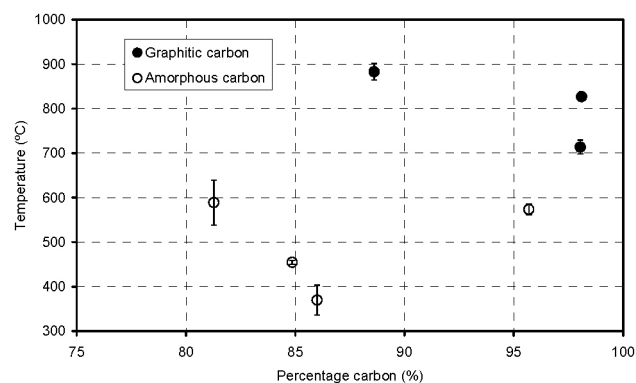


Figure 4. Peak CO₂ emission temperature against percentage carbon in sample

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