

A Novel Technique for Investigating the Nature and Origins of Deposits Formed in High Pressure Fuel Injection Equipment

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ABSTRACT

Recent developments in diesel fuel injection equipment coupled with moves to using ULSD and biodiesel blends has seen an increase in the number of reports, from both engine manufacturers and fleet operators, regarding fuel system deposit issues. Preliminary work performed to characterise these deposits showed them to be complicated mixtures, predominantly carbon like but also containing other possible carbon precursor materials. This paper describes the application of the combination of hydropyrolysis, gas chromatography and mass spectrometry to the analysis of these deposits. It also discusses the insights that such analysis can bring to the constitution and origin of these deposits.

INTRODUCTION

The compression ignition, internal combustion engine that is now commonly referred to as the diesel engine was in fact in existence before Rudolf Diesel filed his patent in 1892 (1). What Diesel claimed in his patent was that efficiency improvements could be made to the reciprocating internal combustion engines by adding the fuel such that energy was released at constant pressure thus reducing peak temperatures and concomitant heat losses to the combustion chamber walls. Over a century later the diesel engine is still favoured for its efficiency when compared to the spark ignition engine.

However, the major reasons for this efficiency benefit are that the diesel engine can operate at higher compression ratios and has reduced pumping losses.

Despite the greater efficiency of the diesel engine it had a lower power density, was noisier and "dirtier" than a spark ignition engine; the latter therefore found greater favour for automotive applications especially at the lighter end of the market where the weight of the engine was a more significant factor. However with over a century's development of fuel injection equipment it is now possible to deliver the fuel to the combustion chamber of a diesel engine in a very precise manner to overcome many of these perceived negatives of the diesel engine.

Successive tightening of permissible emissions limits along with recent concerns over ever increasing levels of carbon monoxide (CO₂) emissions has accelerated the development of fuel injection equipment (FIE) leading to ever higher fuel injection pressures and ever smaller fuel injection orifices. These ever more sophisticated FIE systems require ever more precisely controlled and consistent fuels to ensure their satisfactory operation.

Fuel specification however is not solely dictated by the requirements of the FIE. Engine fuels are always a compromise between what the engine designers consider an ideal fuel and what the petroleum refiners

can produce at a reasonable price from the crude oil from which they start. Environmental considerations also come into play. This is evident in the successive reductions in the allowable sulphur content of fuels. High fuel sulphur not only contributes to the formation of sulphuric acid emissions (acid rain), it also contributes to the mass of particulate matter emitted and can rapidly damage exhaust aftertreatment devices designed to reduce other regulated pollutant emissions. More recently due to concerns over net CO₂ emissions and security of supply there is growing pressure to include renewable source components into the fuel. For diesel fuel the current focus is on the inclusion of fatty acid methyl esters (FAME) other wise known as bio-diesel.

Due to the fact that in a diesel engine fuel is injected directly into the combustion chamber the FIE is inevitably exposed to the high temperatures and pressures of the combustion chamber along with the liquid and gaseous components of the combustion process. This has always resulted in some degree of deposit formation associated with the FIE. As the FIE becomes more sophisticated and the demands upon it for engine performance become greater, the sensitivity to deposit build up and the need to control it must also increase. In the 1980s the first internationally recognised test procedure was developed to assess the propensity of fuels to form deposits on the injection nozzles of diesel FIE (2). This procedure used a 1.9 litre indirect injection (IDI) that was commonly found in passenger cars of the time and had been shown to correlate with field experience.

This was closely followed by the development of a procedure to assess the propensity of fuels to form deposits on a heavy duty automotive diesel engine (3). Until 2008 these were the only two universally recognised and approved methods for testing diesel fuels to ensure that they were fit-for-purpose. The engine technology used in these tests is now restricted to the legacy fleet and they are not considered appropriate for the latest generation of diesel engines. To combat this various researchers have been working to develop a procedure to assess the fuel performance using the latest technology FIE. A number of technical papers were published detailing this work before the method was finally approved in 2008 (4).

Many of the technical papers (5-7), show that deposits are promoted by the inclusion of an organic zinc compound in the test fuel. However, another paper by the same authors (8) detailing an extended distance field trial showed no zinc to be naturally present in the fuel as sourced or in the fuel remaining in the vehicles fuel tank. Another paper (9) highlights that the morphology of deposits is dependant on the engine operating regime. The inclusion of biodiesel into the fuel has also shown an increased propensity to cause fouling of the fuel injection system, both in the fuel injectors (10) and the fuel filters (11). It is thus essential that we fully understand the nature of these deposit in order to

ensure that test procedures designed to evaluate whether a fuel is fit for purpose will in fact produce deposits representative of those found in the field.

Much research has been conducted into the degradation pathways of different hydrocarbon fuels that may lead to deposit formation. Some of this work has considered single component hydrocarbons (12-14) whilst many have looked at the multi-component jet fuels (15-17) that have to perform in a more arduous environment than many current diesel fuels. Work has also been done on diesel fuel (18-20) and more recently the FAME found in biodiesel blends (21).

These mechanisms can be demonstrated in the laboratory and the reaction products can be found in fuel samples taken from the field. However, in order to be certain that the proposed mechanisms are what is leading to the observed deposits it is again essential that we can fully characterise the deposits.

Many techniques are available and have previously been used to characterise the depots in FIE. 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 a detergent which will be attracted to the deposit. It is therefore only to be expected that the detergent will be found on the deposit. This has often led to the erroneous conclusion that the detergent is in some way responsible for the deposit.

Hydropyrolysis, otherwise know as *hypy*, has been successful in characterising carbonaceous material in coal, oil, and meteorites but has not previously been considered for trying to characterise deposits formed from diesel fuel in FIE. This paper describes the technique and demonstrates how it has been applied to the characterisation of deposits that are currently causing problems in both fuel filters and fuel injectors in conventional field applications.

THE TECHNIQUE

Hydropyrolysis refers to pyrolysis taking place under an atmosphere of high hydrogen pressures; hydrogen pressures of greater than 10 MPa are typically used. The technique has been developed for its unique ability to release high yields of bound biomarkers from petroleum source rocks, heavy oil fractions (22), meteorite carbonaceous deposits (23) and coal (24) whilst minimising the structural rearrangement of those deposits. In relation to deposits formed in diesel engines hydropyrolysis has the capability to identify particular chemistries from the hydrocarbons released.

A sample of the deposit to be analysed was mixed with a sulphided molybdenum catalyst and placed in the hydropyrolysis reactor on top of a bed of fresh catalyst. The reactor was first heated rapidly from ambient temperature to a temperature representative of the lower

end of the boiling curve of adsorbed hydrocarbons (for example, 250°C) to remove any adsorbed material.

The reactor was then heated more slowly to a temperature at the upper end of the boiling curve, for 350°C. A high pressure hydrogen gas flow is maintained through the reactor and any products evolved are swept into a dry ice cooled silica trap. After cooling the rig, fresh silica is placed in the trap and the sample is subject to hydrolysis. This is accomplished by rapidly heating the reactor to the final temperature of the desorption phase and then slowly heating the reactor to the final temperature of greater than 500°C. The reactor is then held at this temperature for a couple of minutes with the evolved products again being trapped in the cooled silica trap. The experimental set up is shown schematically in Figure 1.

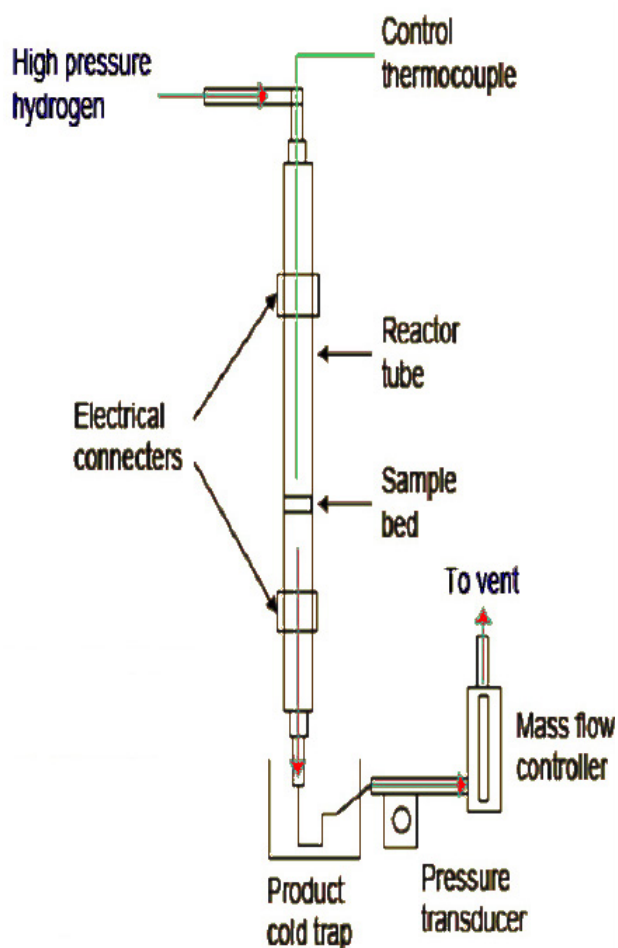


Figure 1. Schematic diagram of hydrolysis rig

It should be noted that it is a limitation of *hypy* that it will only release products from lightly cross linked material and not large semi-graphitic layers. As such it is not a panacea analysis but one which provides valuable insights into the complex deposit characterisation problem.

EXPERIMENTAL PROCEDURE

A number of 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 filters were plugged with a black carbonaceous deposit. Many of the fuel filters presented for analysis were "fuel wet" and an analytical protocol was developed to enable the separation and characterization of both the soluble and insoluble moieties. The protocol is described in reference (25). In this paper, it was only the solid residue that was evaluated. The full protocol as described in reference (25) is illustrated schematically in Figure 2. The sections of the protocol relevant to the hydrolysis technique are shown in the white boxes with the remainder of the protocol shown in grey boxes.

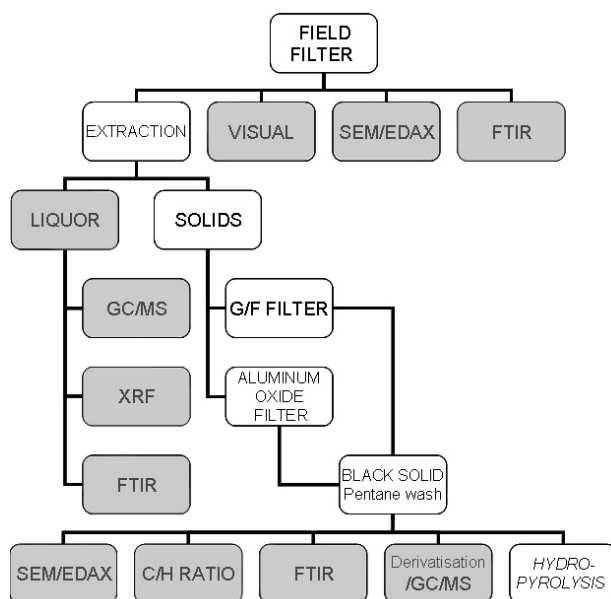


Figure 2. Analytical Separation Protocol.

A 15cm by 3cm section of the filter element was cut from the fouled fuel filter. The filter section was initially weighed to allow determination of the mass of residue. The filter section was then subjected to visual analysis; scanning electron microscopy with energy dispersive X-ray analysis (SEM/EDAX); and Fourier Transform Infra-red analysis (FTIR). The deposit was then extracted with HPLC (High Pressure Liquid Chromatography) grade tetrahydrofuran (120mL), either by placing in an ultrasonic bath for 15 minutes, or by soaking overnight. The liquor was then filtered through a glass fibre filter (8µm) or an aluminium oxide membrane (0.2µm). The filtrate was washed in pentane (40mL) to remove any remaining diesel fuel and subjected to SEM/EDAX; carbon/hydrogen ratio analysis; FTIR; derivatised gas chromatography with mass spectroscopic detection (GC/MS); and hydrolysis.