

Injector Fouling Performance and Solubility of GTL Diesel Dosed with Zinc

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ABSTRACT

The success of modern diesel passenger cars is, to some extent, attributable to the advent of common rail diesel injection technology. Today almost all new diesel engines use this technology which is characterised by high fuel injection pressure and very small diameter nozzle holes. The industry rapidly developed a new test procedure to assess a fuel's propensity to cause injector fouling and also to assess the ability of additives to clean and to keep such injectors clean. The CEC F-98-08 DW10 test procedure was approved in March 2008 by the CEC and is now considered an industry standard test method. The test method requires 1ppm zinc to be dosed into all test fuels in order to accelerate injector fouling.

This paper presents DW10 test results for gas-to-liquids (GTL) diesel. A similar test method, using a different engine, was developed in-house and showed good correlation with the DW10 test. The results confirm a significantly different response with GTL diesel compared to regular diesel when both have been dosed with zinc. A series of chemical laboratory test work investigated the solubility of zinc in GTL. The results reveal that, when compared to EN590 diesel, zinc more readily drops out of a GTL-zinc solution, prepared in a similar way to that used in the DW10 test. It was also found that zinc is less readily taken up into solution with GTL from solid zinc components than it is by EN590 diesel.

The lower solvency of GTL diesel results in greater injector deposit formation due to zinc drop-out in the DW10 test method. Zinc pick-up tests, however, demonstrate that GTL diesel is less likely to pick up zinc in the logistic chain in the market. It is shown that various deposit control additives are very effective in preventing deposit formation in a GTL-zinc solution and have the ability to clean up zinc-fouled injectors.

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INTRODUCTION

It is well known that trace amounts of zinc, dissolved in diesel fuel rapidly accelerate injector nozzle fouling in modern common rail diesel engines [5,6,24]. These deposits adhere to the metal surfaces inside the very small holes of the injector nozzle, thereby reducing the fuel flow into the engine which ultimately results in a loss of engine power.

This is the basis for the CEC F-98-08 DW10 injector fouling engine test procedure which has become an industry standard since March 2008 [8]. A 1ppm zinc solution is required by the method to be dosed into all test fuels in order to accelerate injector fouling. Sasol has been conducting injector fouling research on GTL diesel for many years using an engine test method very similar to the DW10 test. Without the deliberate addition of zinc to the test fuel, GTL diesel performs very well in terms of injector cleanliness when

compared to petroleum-derived diesel. This improvement has been shown to be significant for neat GTL as well as for blends of GTL and EN590 diesel in both new and old technology diesel engines. The injector cleanliness benefits of GTL diesel have been linked to the higher thermal stability of this fuel [3,11]. A detailed study of the properties and injector fouling performance of the neat GTL and EN590 base fuels (without zinc) as well as a comprehensive range of binary blends of the two was covered in a previous paper by the same authors [11].

When GTL diesel was tested using the CEC F-98-08 DW10 test method, the results were very different. The effect of adding 1ppm zinc to the fuel resulted in much higher levels of injector fouling than the petroleum-derived reference fuel. While it has been shown that deposit control additives are still effective with GTL diesel [3],

understanding why zinc would affect GTL diesel differently to petroleum-derived diesel is important.

It should be borne in mind that the DW10 test procedure measures the effect of zinc on injector deposits and can therefore be heavily influenced by the ability of a fuel to keep zinc in solution. With a worldwide trend towards alternative sources of diesel fuel, it is possible that fuels of varying solvency will enter the market. The effect of fuel properties, such as solvency, on established industry test methods must be carefully understood so that the results can be interpreted in a way that is relevant to performance in the market.

It is known that the solvency of GTL diesel is lower than that of conventional diesel due to the very paraffinic nature of GTL diesel. GTL diesel has negligible aromatic content [2]. The ability of GTL diesel to hold zinc in solution is conceivably somewhat different to other fuels and is the subject of the research undertaken here.

BACKGROUND

In modern common rail fuel injectors, it is difficult to repeatably measure fouling of the nozzle holes. The reason for this is that the mechanism of deposit formation typically involves thermal condensation and cracking of the hydrocarbon fuel at the very high temperatures to which the nozzle is exposed. Deposit formation is exacerbated when nozzle temperatures exceed 300°C [23]. Such deposits are typically carbonaceous and are unable to bond very strongly to the metal surfaces of the injector nozzle holes. With fuel pressures in excess of 1600 bar and holes with diameters around 130 μm , the flow conditions can be considered extreme in terms of fluid velocity and temperature. Deposits can therefore break away and build up sporadically, usually never building up substantially enough to cause a measurable flow reduction. However, if zinc is dissolved into the fuel in a concentration as low as 1ppm the fouling mechanism becomes very different. Ikemoto et al describe the coking mechanism when zinc is present in the fuel [24]. The main factors resulting in deposit formation are the presence of zinc in the fuel, exposure to lower carboxylic acid in the combustion gas and high temperature. In their experiments the highest nozzle tip temperature was measured as 230°C at the maximum power point of a typical passenger car common rail diesel engine, and this was the point at which fouling was most severe. Initially lower zinc carboxylate is formed close to the injector nozzle hole outlet by reactions between the abovementioned factors. The zinc carboxylate deposit at the hole outlet grows by a further reaction with CO_2 in the combustion gas to form zinc carbonate which steadily grows along the length on the nozzle hole towards the inlet of the hole. These zinc deposits are able to bond to the metal surfaces far more strongly than carbonaceous deposits and the deposit is able to build up and restrict fuel flow, despite the high shear forces experienced. These deposits can be removed by cavitation induced erosion which depends on nozzle hole geometry [24]. Additive chemistry is also

effective in the prevention of such deposit formation and dissolving existing deposits [5,8].

Engine testing was conducted by Sasol to investigate common rail injector fouling. It was found that fuel flow dropped substantially initially and continued to decline the longer the engine was run on zinc-containing fuel, indicating that the deposit was continuously building up in the injector nozzle hole. A physical analysis of an injector nozzle was conducted after such an engine test. This nozzle was carefully sectioned through one of the nozzle holes. Scanning electron microscopy (SEM) was used to view the deposits and conduct elemental analysis of the area where the deposit had built up.

Figures 1 and 2 show the sectioned nozzle that was run on an EN590 diesel fuel containing 1ppm zinc for 16 hours in an engine test method similar to the DW10, using a Euro 3 engine with solenoid type common rail injectors. Fuel flow was restricted by over 3% by the end of the test.

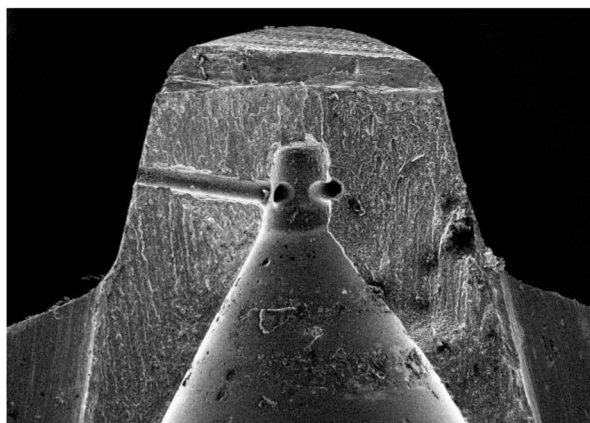


Figure 1. SEM image of a sectioned injector nozzle tip

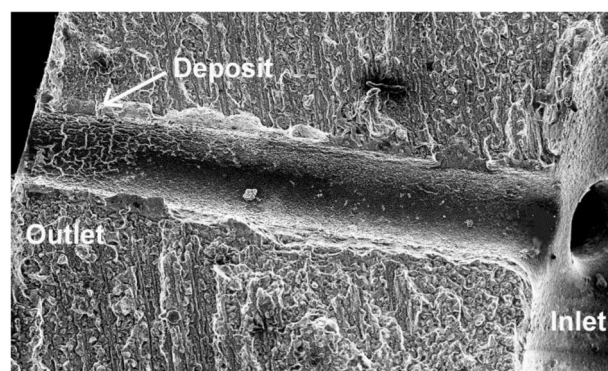


Figure 2. Close-up SEM image of the sectioned nozzle hole

The deposit can be seen in Figure 2 and is more established near the outlet of the nozzle hole where the fuel enters the combustion chamber. This is also the area where hot combustion gases may enter the nozzle hole after injection has stopped. This corresponds to the initial phase of

zinc carboxylate deposit formation as described by Ikemoto [24]. Elemental analysis, shown in Figure 3, was conducted on this area of the nozzle hole using energy dispersive spectroscopy (EDS). Significant amounts of zinc were measured in the deposit. This has also been seen by other researchers. [4,6,24]

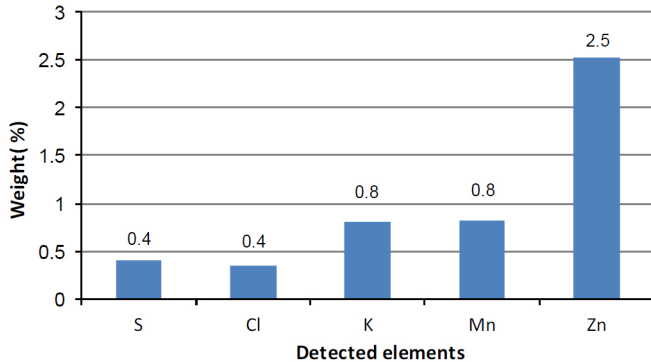


Figure 3. Elemental analysis of the injector deposit surface

An analysis of the base metal was done and these elements have been subtracted from results in Figure 3. It was also found that no zinc was detected in the deposit of injectors that were tested in a similar way with neat diesel fuel, i.e. without zinc addition.

This is indicative of the fact that zinc, which is dissolved in the fuel, drops out of solution, reacts with combustion gasses and causes deposit formation. It makes sense that fuels which are able to hold zinc in solution will mitigate the rate of zinc related deposit formation. It can be questioned whether zinc in diesel is relevant in the market. In most cases it is not, however in some cases it has been shown that fuels may pick-up zinc in the market logistic system, e.g. when fuels come into contact with galvanised pipes and fittings.

In a previous study, Leedham et al. [4] showed that, in a similarly fouled injector hole, the deposit contained zinc. They also showed that fuel composition can affect the propensity for zinc uptake in the market. In this case the effect of various lubricity improver additives was investigated. It was shown that significant amounts of zinc could be dissolved in fuel using a laboratory immersion test with zinc metal powder. During a vehicle field trial, they observed that zinc could be picked up from certain vehicle fuel tanks when acid-based lubricity improvers were added to the test fuel. Furthermore metal uptake was greater when daily fuel consumption was low and fuel spent more time in the fuel tank.

Quigley et al. [7] found that trace metal contamination at European forecourts was negligible. They came to the same conclusion with vehicle trials where a number of vehicles did not pick-up zinc from the internal fuel system. In separate tests where diesel fuels were exposed to zinc powder, significant amounts of zinc were taken up. Quigley et al. [7] pointed out that the only realistic source of zinc in the market

is galvanized components. Inconsistent findings relating to zinc contamination in market diesel has led to debate over the relevance of the DW10 test procedure [8]. It is, however, not disputed that if zinc is dissolved into market diesel, this would cause an injector fouling problem. Although unlikely on a large scale, zinc contamination in diesel is possible and thus of concern as it may result in market failures.

Deposit control additives (DCA) have been developed to effectively combat zinc-related injector fouling. Many of these additives are also very effective at dissolving the deposits from previously fouled injectors [5,6,8]. The efficacy of these additives does mean that any potential zinc-induced problem can be eliminated if they are used routinely.

The subject of solvency is particularly relevant here. In order for a chemical species (solute) to be dissolved by a solvent, the solution needs to be in a lower free energy state than the separate solute and solvent. This requires that the solute molecules/atoms are surrounded by solvent molecules in a process called solvation. The ability of a solvent to keep a solute in solution is called its solvency and is typically applied to the ability of a hydrocarbon solvent to keep polar solutes in solution [17]. Solvation is promoted when the interaction energies between solvent and solute molecules are similar to those between solvent molecules. Thus non-polar solutes are readily solvated by non-polar solvents while polar solutes prefer polar solvents. Metals are dissolved by solvents that are characterized, not just by dispersive (London and van der Waals) interactions, but by stronger interactions [12]. Among hydrocarbon species, aromatic compounds are most likely to display stronger interactions unlike saturated paraffins which have only dispersive interactions. This is because of the uneven distribution of charge around the aromatic ring [18].

Metals may also be retained in an organic solution by a process known as chelation. In this case, a salt is formed. This involves a very strong reaction of an organic molecule which contains a polar group(s) which stabilizes the metal ion in solution. These groups often contain oxygen, nitrogen and/or sulphur atoms. The chelating molecule usually has a less polar region which is solvated by the organic solvent, thereby retaining metal in solution. Many deposit control additives work by this mechanism and zinc neodecanoate is also a chelate.

Because the absence of aromatics imparts a lower solvency to GTL diesel than EN590 diesel, GTL diesel would, firstly, retain less zinc in solution when dosed with a zinc compound but, secondly, would pick up less zinc when GTL and EN590 diesel are exposed to metallic zinc. The lower solvency of GTL diesel towards zinc would mean zinc is less likely to be taken up into solution and thereby contaminate the fuel than higher solvency diesels. These hypotheses are investigated in detail in the following sections.

TEST FUELS

This study focuses specifically on the effect of zinc in GTL diesel and the results presented originate from three different test projects. The first involves DW10 engine tests, the second uses a similar in-house engine test method and the third is a series of chemistry laboratory tests. These test projects use different test fuels but are all based on the same base fuels. The reference fuel was a conventional petroleum-derived diesel fuel which conformed to current European EN590 specifications for sulphur free diesel and contained only a lubricity improver additive. The one exception here is for the CEC F-98-08 engine tests where the reference fuel is specified to be Haltermann DF 79-07 by the test procedure. This fuel is also petroleum-derived and conforms to EN590 specifications.

GTL diesel was obtained from ORYX (Pty Ltd) in Qatar and represents a typical GTL summer grade diesel with a CFPP of around -8°C . The GTL diesel fuel was a highly paraffinic diesel fuel with negligible aromatic species or sulphur and a high cetane number. During the manufacture of this diesel, natural gas is reformed to synthesis gas, which is then subject to low temperature Fischer Tropsch (LTFT) catalysis and subsequent refining to fuel products. The production process and properties of GTL diesel fuels have been described in more detail in previous publications [1,2,3]. It is important to note that the cold flow properties of GTL diesel may be altered significantly by changing the degree of isomerisation and distillation cut points, to achieve significantly improved cold flow properties, for applications in colder climates.

Rapeseed methyl ester (RME), as blended with GTL diesel in [table 3](#), was obtained from SBE Bioenergie (SBE Bioenergie, Saarbrücken, Germany). The neat FAME was evaluated and complied to EN 14214 specifications [16].

The details of the fuels used for each of the three sets of results, presented in this study, are shown in [Tables 1,2,3](#):

The fuel properties of the base fuels used in this study are given in [Appendix 1](#).

Table 1. Test fuels for CEC F-98-08 DW10 engine tests

Fuel Name	% GTL	% EN590	Additives
DF 79-07 Zn	0	100	1ppm Zn + unknown LIA*
G20E80 Zn	20	80	1ppm Zn + LIA in GTL**
GTL Zn	100	0	1ppm Zn + LIA**
GTL Zn DCA	100	0	1ppm Zn + LIA** + DCA***

* Lubricity improver additive

** Commercial ester-based lubricity improver additive, 200ppm

*** Commercial deposit control additive, 200ppm

Table 2. Test fuels for Sasol Common Rail Injector Fouling Engine tests

Fuel Name	% GTL	% EN590	Additives
EN590 Zn	0	100	1ppm Zn + Unknown LIA*
EN590 DCA	0	100	DCA + Unknown LIA*
GTL Zn	100	0	1ppm Zn + LIA**
GTL DCA	100	0	LIA** + DCA***

* Lubricity improver additive

** Commercial ester-based lubricity improver additive, 225ppm

*** Commercial deposit control additive, 390ppm

Table 3. Test fuels for chemistry studies

Fuel Name	% GTL	% EN590	Additives
EN590 Zn	0	100	1ppm Zn Unknown LIA*
G20E80 Zn	20	80	1ppm Zn + LIA in GTL**
G80E20 Zn	80	20	1ppm Zn + LIA in GTL**
GTL Zn	100	0	1ppm Zn + LIA in GTL**
GTL Zn DCA	100	0	1ppm Zn + LIA** + DCA***
GTL Zn RME	93	0	1ppm Zn + LIA** + RME****

* Lubricity improver additive

** Commercial ester-based lubricity improver additive, 225ppm

*** Commercial deposit control additive, 390ppm

**** Rapeseed methyl ester, 7%

EXPERIMENTAL

The methodology used in the various experiments is described in some detail below.

Engine Test Methods

CEC F-098-08 DW10 common rail injector fouling test method

The test was performed according to the CEC F-98-08 (Issue 3) procedure. This test method is designed to evaluate the propensity of diesel or diesel additive formulations to prevent deposit formation in injector nozzle spray holes. A PSA DW10BTED4 engine is used. This is representative of modern European high speed direct injection diesel engines and is capable of meeting Euro 5 emission legislation. The engine has a Siemens VDO piezo common rail fuel injection system operating at pressures up to 1600bar.

A new set of injectors is used for each test. These are run-in for 16h prior to the test commencing, using the DF 79-07 EN590 reference fuel which does not cause fouling. The test procedure consists of alternating sequences of 8h of engine operation and 8h of engine stopped. The test duration is 56h, of which the engine is running for 32h. The 1h cycle as shown in [Figure 4](#) is repeated during engine operation.