

Possible Mechanism for Poor Diesel Fuel Lubricity in the Field

Stephen Cook, Jim Barker, Jacqueline Reid and Paul Richards
Innospec

ABSTRACT

Traditionally, diesel fuel injection equipment (FIE) has frequently relied on the diesel fuel to lubricate the moving parts. When ultra low sulphur diesel fuel was first introduced into some European markets in the early 1980's it rapidly became apparent that the process of removing the sulphur also removed other components that had bestowed the lubricating properties of the diesel fuel. Diesel fuel pump failures became prevalent. The fuel additive industry responded quickly and diesel fuel lubricity additives were introduced to the market. The fuel, additive and FIE industries expended much time and effort to develop test methods and standards to try and ensure this problem was not repeated. Despite this, there have recently been reports of fuel reaching the end user with lubricating performance below the accepted standards. Recent publications have also suggested that it is not uncommon for sodium hydroxide used in the fuel refining industry to be present in fuel entering the supply chain downstream of the refinery. Due to the chemical nature of some lubricity additives there is clearly the possibility of interaction.

This paper briefly reviews the need for diesel fuel lubricity improver additives, previous work on such additives and possible interactions. It then goes on to present new work performed to investigate how the presence of sodium compounds in the fuel may affect the performance of a range of lubricity additives of different chemistries. It shows that the presence of the sodium hydroxide can lead to reactions with and hence the depletion of certain types of lubricity additive. This could inevitably lead to reduced lubricity performance and fuels reaching the customer that do not meet specification.

CITATION: Cook, S., Barker, J., Reid, J. and Richards, P., "Possible Mechanism for Poor Diesel Fuel Lubricity in the Field," *SAE Int. J. Fuels Lubr.* 5(2):2012, doi:10.4271/2012-01-0867.

INTRODUCTION

The issue of diesel fuel lubricity, or the lack thereof, was highlighted [1] in the early 1990s when Sweden enacted legislation mandating the reduction of fuel sulphur and aromatic content to a maximum of 50 mg/kg and 20 % respectively for Class 2 diesel and to a maximum of 10 mg/kg and 5 % respectively for Class 1 diesel. Earlier work investigating the effect of fuel sulphur levels on engine deposits and wear [2, 3, 4, 5] had suggested that high sulphur fuels resulted in increased wear. It may therefore initially be supposed that removing sulphur from the fuel might reduce wear. However, the way in which fuel sulphur content was influencing wear rates was due to the presence of sulphur trioxide [3, 4] as a result of combustion rather than the presence of sulphur compounds in the fuel affecting the lubricating properties of the fuel. Poor housekeeping resulting in "stagnant water bottoms in fuel storage tanks which contained rust, sea water, and sulphate reducing bacteria" was also found to cause corrosion in aircraft fuel systems [6]. Probably due to the fact that diesel fuel in the 1940s and 50s

was predominantly straight run distillate; the intrinsic lubricating ability of diesel fuel was never questioned.

However, history had issued a warning. Awareness of the importance of fuel lubricity had been raised in the 1950s within the aircraft engine community. The high temperatures that prevailed in certain aircraft applications [7, 8] had driven the requirement for increased fuel stability and in many cases this was brought about by increased refining of the fuel. This increased refining commonly utilised hydrotreating [9, 10] which had been shown to be beneficial [8]. Hydrodesulphurisation had been introduced to "sweeten" the increasingly common high sulphur fuels that were being produced. It is commonly thought that removing the sulphur compounds reduces the fuels lubricity, however, the hydrotreatment not only removed sulphur compounds but it also removed other polar compounds containing nitrogen and oxygen plus heavier aromatic compounds. Work by Appeldoorn and Tao [11] concluded that heavy aromatic compounds, rather than sulphur compounds per se, were responsible for imparting lubricity to the fuel. Work by Nikanjam [12] had actually shown that adding sulphur compounds back into low sulphur fuel could have a negative

effect on fuel lubricity. Earlier work by Appeldoorn and Dukek [13] had concluded that "Certain additives such as corrosion inhibitors have a marked effect on lubricity. At very low concentrations these additives reduce friction and wear, while at high concentrations they reduce gear scuffing; that is, they improve load carrying capacity." These corrosion inhibitors were often organic acids [14, 15]. As regards diesel fuel, work by Wei and Spikes found that polyaromatics, particularly oxygen-containing components reduced wear [16]. Work by Vere suggested that it was the polar compounds that were important contributors to a fuels lubricity [17].

There was inevitably many studies performed around this time to determine the most appropriate method for assessing the lubricity of the fuel. Whilst field trails and fleet tests are the ultimate arbiter of performance these are obviously costly both in terms of finance and time. Rig tests utilising susceptible fuel pumps were also developed [18, 19]. Bench top test that simulated the wear mechanisms without having to utilise the actual fuel pump and thus requiring significantly lower quantities of fuel were clearly more desirable and many alternatives were developed. These have included the Ball On Cylinder Lubricity Evaluator BOCLE [20] and variations of this method such as [21] and the Scuffing Load Ball-On-Cylinder Lubricity Evaluator (SLBOCLE) [22]. Other test methods have included using the Cameron Plint TE77 [23], the Thornton Aviation Fuel Lubricity Evaluator (TAFLE) [24, 25] and the Ball on Three Disks (BOTD) [26]. The High Frequency Reciprocating Rig (HFRR) which had been developed for other engine tribological investigations was also investigated for assessing the lubricity of Diesel fuels [27]. After a significant programme of work [28] the HFRR is now widely accepted as a representative measure of diesel fuel lubricity and has become a standard test method [29]. Alternatives such as the roller on cylinder lubricity evaluator (ROCLE) have since been proposed [30].

It must be remembered that the whole issue of diesel fuel lubricity has come about through increased refining of the crude oil to produce the high quality diesel fuel that the modern customer and legislation demand. Particularly in the US part of this refining process is the use of caustic washing to remove the acidic compounds generated as part of the desulphurisation process. The caustic used in this process should obviously be removed before the finished fuel is released from the refinery. With the good housekeeping we expect from refineries in the US this is evidently so. This provides the possibility of interaction between the caustic and fuel additives resulting in fuel injector deposits. A fuller discussion of this phenomenon is outside the scope of this paper but is discussed more fully in [31].

If there is a possibility of sodium hydroxide entering the fuel supply chain, and inevitably documentary evidence of this is hard to come by, then the obvious question is how this caustic material will react with carboxylic acid materials that may be used to meet the lubricity specification required by the advanced fuel injection equipment employed on modern

engines. The work presented here is from a programme designed to investigate how the presence of different sodium compounds which could enter the fuel system, could interact with different lubricity improver additive chemistries. The potentially disastrous consequence of allowing sodium hydroxide to enter the fuel system when only carboxylic acid lubricity improvers are used is clearly demonstrated.

EXPERIMENTAL PROCEDURES

To test the hypothesis that the effectiveness of the lubricity improver additive could be compromised by the presence of sodium compounds within the fuel, a series of lubricity performance tests were conducted before and after the potential interaction with the sodium compound. Different lubricity improver samples and chemistries were tested and the sodium ions were added as either sodium hydroxide or sodium chloride and in both cases as an aqueous solution. As aqueous solutions are immiscible with diesel fuel a high shear blender was used to ensure good contact between the phases and some additional tests were performed after the samples had been allowed to stand for a short time. The various elements of the procedure are described in more detail in the following subsections.

TEST FUELS

Base Fuel

All the test work reported here was carried out using a European reference fuel; RF06. As this reference fuel must meet the European standard EN590, the fuel would normally contain a lubricity improver additive. The fuel must therefore be purchased from the producer before the lubricity improver additive is added or the fuel sample must be processed to remove the additive. For this work the base fuel was clay filtered to ensure that no lubricity improver additive was present. This approach also ensured that any other polar compounds that might confuse the results were removed. A copy of the certificate of analysis of the base fuel before clay filtering is included in [Appendix A](#). A copy of the procedure for clay filtering the fuel is included in [Appendix B](#).

Lubricity Improver Treat Rate

Two commercial carboxylic acid lubricity improver additives from different suppliers were used; designated acid LI (A) and acid LI (B). Both of these additives are tall oil fatty acid (TOFA) based products. An ester based additive was also tested to assess the effect of a different chemistry. The lubricity performance of diesel fuel is specified as a maximum wear scar diameter (WSD) of 520 μm in D975 and 460 μm in EN590; the repeatability of the HFRR method is given as 63 μm in ISO 12156-1:2000. The treat rate of the lubricity improver additives was thus chosen to give a target WSD of 397 μm to comply with both the D975 and EN590 limits even when allowing for the results being at the favourable limit of the repeatability range. A treat rate of 100

mg/L was thus chosen for the carboxylic acid lubricity improver additives and 300 mg/L for the ester based additive.

Sodium Hydroxide Addition

An aqueous solution of sodium hydroxide, as a 17.3 wt% solution, was prepared by accurately weighing out an excess of solid sodium hydroxide into a suitable, tared vessel and then adding to it the appropriate mass of de-ionised water. Such a solution contains 9.95 wt% sodium ions. This aqueous solution was then used at treat rates of either 3mg of sodium per litre of fuel or at 1mol equivalent per acid group on the lubricity improver. For the 17.3 wt% solution 3mg of Na gives 25mg of water. For non-acid lubricity improvers, such as esters or amides, the 1 mol equivalency has been determined as one equivalent per acid group of the parent carboxylic acid from which they may be regarded as being derived. For the 1mol equivalent tests the mass of sodium hydroxide solution required is calculated from the following formula:

$$M_{OH} = 4000 * N_{acid} / C_{OH} \quad (1)$$

Where M_{OH} is the mass of NaOH solution (mg), N_{acid} is the number of acid groups present in mmol and C_{OH} is the concentration of the NaOH solution (%). The number of mols of acid present in the fuel is determined from the following formula:

$$N_{acid} = (F_{vol} * LI_v * C_{LI}) / 1000 * LI_{fwt} \quad (2)$$

Where F_{vol} is the volume of fuel in the sample (cm^3), LI_v is the valency of the lubricity improver (e.g. 1 for a monoacid and 2 for a diacid), C_{LI} is the concentration of the lubricity improver (mg/L) and LI_{fwt} the formula weight of the lubricity improver (Da).

In cases where LI_{fwt} is not known, such as for a complex mixture, e.g. a TOFA, an effective formula weight per acid group (Da_{eff}) can be obtained from the acid value (V_{acid}) as expressed in mgKOH/g using the formula:

$$Da_{eff} = 56,000 / V_{acid} \quad (3)$$

When using this formula it must be remembered that LI_v in equation (2) above becomes unity.

In situations where lubricity improver additive is supplied as a concentrate in inert solvent then it must be recalled that:

$$C_{LI} = C_{add} * C_a / 100 \quad (4)$$

Where C_{add} is the concentration of additive solution in the fuel (mg/L) and C_a is the weight per cent concentration of lubricity improver in the concentrate.

The aqueous solution of sodium hydroxide was added to the diesel fuel and mixed using a Waring Blendor Model

BHL120 with a two minute agitation time at a speed setting of "1" on the Waring Blendor.

Sodium Chloride Addition

For sodium chloride additions a 23.4 wt% aqueous solution was prepared. This ensured an equal water addition for an equal sodium addition in comparison to the NaOH blends. For mol equivalency the NaCl solution was added to give the same mass of sodium as for the NaOH addition.

HFRR TESTING

After blending a sample of the blend was taken and subject to HFRR testing. The blend was then filtered using a Whatman® Glass Microfibre Filter GF/A, 47 mm Ø and another sample taken for HFRR testing. The remainder of the blend was allowed to stand for an hour before being re-stirred and another sample taken for HFRR testing. The stored blend was again filtered and a final sample taken for HFRR testing. Clean glassware was used throughout. A sample of the filtered fuel was then taken for further HFRR testing as required. All of the fuels were tested according to the standard procedure ASTM D6079 [29] with a fuel temperature of 60°C.

RESULTS

The results of adding 3 mg of sodium per litre of fuel of the 17.3% sodium hydroxide solution are shown graphically in Figure 1. The clay filtered RF06 fuel produced a WSD of 603 μm which is clearly outside the limit for both D975 and EN590. When treated with 100 mg/L of acid LI (A) the resulting WSD was 394 μm which is just below our target of 397 μm ; the EN590 limit (460 μm) minus the repeatability of the method (63 μm). After the blend was filtered the WSD was reduced even further; to 255 μm . At present there is no explanation for this. When the sodium hydroxide was added at 3 mg of sodium per litre of fuel and the sample was tested after agitation the WSD had increased to 443 μm . This was still within the EN590 limit and within the repeatability of the method when compared to the result prior to the addition of the sodium hydroxide. After being filtered the result was 491 μm which, although within the D975 limit, was greater than the limit set in EN590 and, even allowing for the repeatability of the method, showed a deterioration on the performance of the fuel prior to the addition of the sodium hydroxide.

After being allowed to stand for an hour, to allow for any further reaction to take place, the fuel was again stirred in the high shear blender and retested after stirring. In this case the performance was 501 μm WSD with an insignificant further deterioration to 508 μm after filtration. These results suggest that there is a reaction between the acid lubricity improver additive and the basic sodium hydroxide solution resulting in depletion of the acid content of the fuel. The non-significant increases in WSD post filtration after either NaOH treatment could be due to experimental variability. Alternatively, it could be that some of the products of reaction are insoluble but may provide some lubricity benefit to offset the effect of