

Interrogating the Surface: The Effect of Blended Diesel Fuels on Lubricity

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ABSTRACT

The lubricating properties of two sustainable alternative diesels blended with ultra low sulphur diesel (ULSD) were investigated. The candidate fuels were a biodiesel consisting of fatty acid methyl esters derived from rapeseed (RME) and gas-to-liquid (GTL). Lubricity tests were conducted on a high frequency reciprocating rig (HFRR). The mating specimen surfaces were analysed using optical microscopy and profilometry for wear scar diameters and profiles respectively. Microscopic surface topography and deposit composition was evaluated using a scanning electronic microscope (SEM) with an energy dispersive spectrometer (EDS). Like all modern zero sulphur diesel fuel (ZSD), GTL fuels need a lubricity agent to meet modern lubricity specifications. It has been proven that GTL responds well to typical lubricity additives in the marketplace. The lubricity of ULSD, GTL and blends of these fuels were significantly improved with the addition of as little as 10% volume of RME, inducing more stable hydrodynamic conditions. Topography measurements showed the formation of a residue when RME was blended in the base fuels and composition analysis indicated a predominately carbon formation on the worn surfaces that correlated with wear scar diameters. On the other hand, the test disc under GTL lubrication showed the smooth and residue free surface. The optimal proportion of blended fuel that created the smallest wear scar diameter was 70% GTL, 20% ULSD and 10% RME.

INTRODUCTION

Since 2005, conventional diesel fuel across Europe has been limited to 50 ppm sulphur as part of strict legislation governing the specification of such fuels. To meet this level requires a process that eliminates not only sulphur but also lubricity-imparting compounds such as polyaromatics and oxygen-containing compounds [1-3], hence desulphurization has a direct effect on the lubricating properties of diesel fuel. Furthermore, the introduction of zero sulphur (ZSD) and very low aromatic fuels have lead to an increase in the failure of fuel injection equipment (FIE) [4], and consequently to the introduction of

lubricity standards to ensure the lubrication needs of the FIE are maintained. The standard test for diesel fuel lubricity is based on the high frequency reciprocating rig and a generated wear scar, which under specified conditions must not exceed 460 μm (European standard [5]) and 520 μm (U.S. regulations [6]).

Further environmental concerns have driven the development of biodiesels and one such branch of fuels are those based on fatty acid methyl esters (FAME). Biodiesels containing a mixture of several fatty acids possess good lubricating abilities that have been shown to protect the sliding surfaces of fuel pumps, injection valves and other moving parts in the FIE [7-8]. Methyl ester fuels have also successfully been used as lubricity enhancers. Numerous studies have investigated the lubricating properties of biodiesel and subsequent fuel blends [4, 7-11].

Rapeseed is the principle crop in Europe for the production of first generation biofuel. Rapeseed methyl ester (RME) has enhanced fuel flow and cloud point characteristics as well as possesses good lubricity that can be used to restore the lubricity of conventional very low sulphur diesel fuel [12]. Matzke et al. [13] examined the tribological performance of RME using a high temperature oscillating rig (HiTOM) and compared these to lubricity results from a high frequency reciprocating rig (HFRR). They found that a 5% addition of RME in ULSD increased the lubricity of the blended fuels dramatically. This is in agreement with the results of Sulex et.al [14] that showed with similar proportions of RME, wear scar diameter decreased twofold relative to the base fuels tested.

Other advantages and disadvantages of first generation biodiesel compared to conventional diesel are well documented [15-18]. In response, in particularly to the deficiencies noted in the above, a new generation of alternative fuels has been developed. One such fuel is the synthetic diesel known as gas-to-liquid (GTL) created using a Fischer-Tropsch (F-T) process.

Table 1 Characteristics of base fuels

PROPERTIES	METHOD	ULSD (D100)	RME (R100)	GTL (G100)
Cetane Number	ASTM D613	53.9	54.7	80
Density at 15°C (kg m ⁻³)	ASTM D4052	827.1	883.7	784.6
Viscosity at 40°C (cSt)	ASTM D445	2.467	4.478	3.497
50% distillation (°C)	ASTM D86	264	335	295
90% distillation (°C)	ASTM D86	329	342	342
LCV (MJ kg ⁻¹)		42.7	39.0	43.9
Sulphur (mg kg ⁻¹)	ASTM D2622	46	5	0.05
Aromatics (%wt)		24.4	-	0.3
C (% wt)		86.5	77.2	85.0
H (% wt)		13.5	12.0	15.0
O (% wt)		-	10.8	-
H/C Ratio (Molar)		1.88	1.85	2.10

F-T fuel is virtually free of sulphur and aromatic hydrocarbons and has a very high potential for realizing a much more favorable NOx/PM trade-off without the commonly observed associated penalties in fuel efficiency [19]. From a lubricity perspective and in common with all ZSDs, F-T fuels need a lubricity agent to meet current lubricity standards and it has been shown that they respond well to typical lubricity additives in the marketplace [20-22].

To meet increasingly stringent emission standards, legislation is being introduced in Europe, requiring a substitution of 10% (v/v) of alternative fuel in conventional fuels [22]. A means of achieving this substitution was suggested by Rounce et al. [23] who studied the effects of ULSD/RME/GTL three-way fuel blends on combustion and emissions characteristics. It is the intention of this report to show the beneficial effect of the lubricating properties of the three-way blends when compared to the base and dual-blend fuel combinations.

EXPERIMENTAL APPARATUS AND TEST PROCEDURE

EXPERIMENTAL EQUIPMENT

Assessment of the lubrication properties of the tested fuels was carried out on a HFRR (PCS Instruments Ltd) according to the EN ISO 12156-1:2006 standard [24]. A humidity and temperature controlled cabinet was employed to provide the laboratory air conditions defined by the standard. At the conclusion of each lubricity test, all components having contacted the test fuels were carefully cleaned using toluene and acetone respectively. The HFRR reported the friction coefficient (μ) and lubricant film concentration (film thickness between contacting surfaces).

Optical microscopy (with a 100x magnification lens) was used to assess the size of the wear scar (WS1.4) on the upper specimen again to the procedure defined by the ISO standard (including a correction factor to account for a standard 1.4 kPa water vapour pressure). All of the lubricity experiments were repeated twice and if a difference in corrected wear

scar diameters obtained from the same fuel was higher than 20 μ m, then the test was repeated as defined in [25].

The tribological damage on the lower specimen was assessed using a Talysurf-120 profilometer for the profile of wear scar and topologically using a Philips XL-30 scanning electron microscope (SEM). This in turn was fitted with an Oxford Instruments INCA energy dispersive spectrometer (EDS) system to allow chemical and elemental analysis of the worn surfaces. A SITA pro-line T15 tensiometer was employed to assess intermolecular attraction in the blended fuels.

FUELS

The three test fuels comprised of conventional ULSD, RME and GTL as F-T fuel. The ULSD and GTL are supplied with additives to keep the corrected wear scar diameter below the limitation required by EN 590. The basic properties of the test fuels are given in Table 1. The fatty acid profiles of the RME are given in Table 2 and were analysed according to EN 14103 using a Perkin Elmer Clarius 500 chromatograph coupled with a flame ionization detector.

Table 2 Fatty acid profile of rapeseed methyl ester

Methyl esters	% wt
Palmitic C16:0	4.51
Stearic C18:0	1.47
Oleic C18:1	63.12
Linoleic C18:2	19.85
Linolenic C18:3	9.03
Gadoleic C20:1	0.55
Erucic C22:1	1.47

TEST CONDITIONS

A series of six lubricity tests were conducted. The first focused solely on the base fuels by way of a benchmark for the blended fuel tests. The second to the fourth tests were conducted using dual blends viz. ULSD/RME, GTL/RME and ULSD/GTL with a 10% (v/v) increase of the second fuel to study the effect of blend volumes on lubricity. The fifth and sixth series focused on three-way blends where the content of the principle fuel (i.e. ULSD and GTL) was fixed at 70% with the proportion of RME varied at 5%, 10%, 15%, 20%, 25% and 30% (v/v). A summary of the tests is shown in Figure 1.

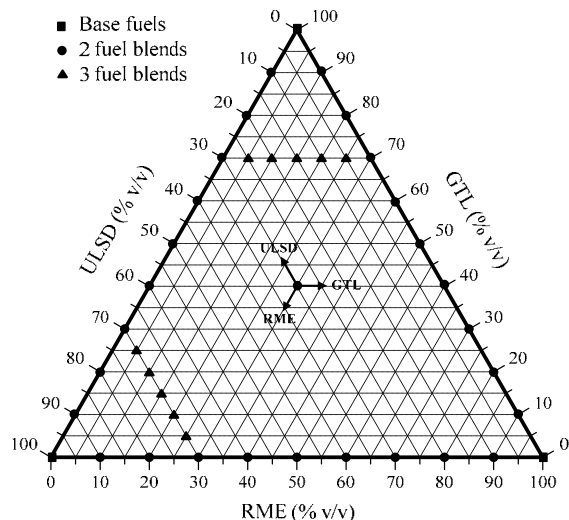


Figure 1 Ternary diagram representing tested blends

RESULTS AND DISCUSSIONS

LUBRICATING PROPERTIES

Base fuels

Figure 2 shows the measured tribological properties obtained from the HFRR tests for the base fuels. They show that RME possesses the best lubricity when compared to ULSD and GTL. This is due to the combination of oxygen-containing compounds and a variety of fatty acids in methyl esters being adsorbed on the rubbing surfaces to reduce friction and improve the lubrication film (shown in figure 2(d)).

Dual fuel blends - RME as a lubricity additive

A correlation was obtained between the lubricating properties and the percentage content of RME blended with ULSD and GTL. The mean values and standard deviation of the lubrication film concentration and friction coefficient against RME percentage are shown in Figure 3 (a) for ULSD/RME blends. The lubricant film of the blended fuels fluctuates around 96% and the friction decreases slightly to minimum of 0.116 in pure RME. Figure 3 (b) shows the corrected wear scar diameter. A 10% addition of RME decreased wear scar diameters by approximately

27%. This reduction in tribological damage on the upper specimen was maximized at RME blends of 20%.

The same three tribological parameters for the blends of GTL/RME are shown in Figure 4. Again, a 10% addition of RME is shown to improve the lubricity of GTL significantly. This result is in agreement with others proved that GTL responds well to typical lubricity additives [20-22]. The wear scar diameter for this blends reduced by approximately 100 μm compared to that of the base GTL. This is likely to have been caused by an increase the viscosity and surface tension that can improve fluid film lubrication. To confirm this hypothesis the surface tension of GTL/RME blends were investigated using a tensiometer. The results, shown in Figure 5, demonstrate that the surface tension increased linearly with an increase in the proportion of RME. In addition the mixture of fatty acids of RME can enhance the boundary lubrication by an increase in the polar-containing compounds, leading to improved stability of the lubrication film as shown in Figure 6. The friction coefficient and corrected wear scar diameter became approximately constant after the optimal proportion, 10% of RME in fuel blends, at approximately 0.112 and 210 μm respectively. It is useful to note that the almost all of the GTL/RME blends posed better lubricating ability than that of the ULSD/RME blends. This is likely to be caused by the better compatibility of biofuels to induce fluid film lubrication and form stronger boundary lubrication conditions.

Dual fuel blends – GTL/ULSD

The effect of GTL on the ULSD lubricity was also examined. Figure 7 shows that a 10% blend of GTL with ULSD decreased the lubrication film, directly affecting the corrected wear scar diameter by approximately 9%. The lubricity of the higher blends (above approximately 60%) reverted to behaviour similar to that of GTL. The GTL fuel demonstrated inferior lubricating characteristics when compared to ULSD and no benefit in overall lubricity was evident when the two fuels were blended.

Tri-fuel blends - Synergistic effect of biofuels

To improve the lubricity of blending GTL and ULSD the tribological properties of three-way blends were studied respectively. The results for the ULSD and GTL biased tests are shown in Figure 8 and 9. It can be observed that as little as 5 % RME can improve the lubricity of ULSD/GTL blends dramatically. The lubrication film, which has a direct bearing on the generated wear scar, increased correspondingly from 90% to 97% and 92% to 98% for the 70% fixed concentration of ULSD and GTL. This resulted in a decrease of approximately 36% and 33% of the wear scar diameter for each composition. It can be seen that proportions of RME higher than 10% (v/v) in blended fuels had no significant effect on lubricity. The optimal proportion of the ULSD biased blends that created the smallest corrected wear scar, was 70%