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The lubricity of diethyl ether (DEE)

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NT2014_120: The lubricity of ethers and alcohol-water blends

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Abstract

Recently new fuels for large marine diesel engines appeared (www.spireth.com) OBATE™ (On-Board Alcohol To Ether) consisting of ether, alcohol and water. The potential of these fuels is to reduce the engine emissions environmental impact without increasing the fuel cost. A potential drawback is the lubricity of the fuels. The lubricity is the ability of a fuel to lubricate the diesel engine injection equipment in the boundary lubrication regime. The present work establishes the lubricity of the components of the fuel and their blends. OBATE™ based on ethanol OBATE™E is predicted to be more challenging with regards to the lubricity than OBATE™M, OBATE™ based on methanol. The lubricity levels of DiEthyl Ether (DEE) and DiMethyl Ether (DME) are equivalent and the lubricity difference between methanol and ethanol is also not significant. The impact of lubricity additives is less pronounced in DEE than in DME but the major difference appears when the alcohols are blended with water. Water has by far the lowest lubricity and this is reflected when it is blended with ethanol. Ethanol with as little as five percent water lubricates similarly to water. The same amount of water in methanol on the other hand does not affect the lubricity of the pure alcohol significantly. The dominance of water in water-ethanol blends indicates that even though DEE is also added, ORBATE™E will be a greater lubricity challenge than ORBATE™M.

Keywords: Lubricity, Diethyl Ether, Dimethyl Ether, Methanol, Ethanol

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1. INTRODUCTION

Recently new fuels for large marine diesel engines appeared (www.spireth.com) OBATE™ (On-Board Alcohol To Ether) consisting of ether, alcohol and water. These fuels decrease the environmental impact of the engine emissions without increasing the cost. There are two types of OBATE™: OBATE™M, a blend of DiMethyl Ether (DME), methanol and water and OBATE™E consisting of DiEthyl Ether (DEE), ethanol and water.

Ethanol and methanol have been known as excellent fuels for both gasoline and diesel engines for some time now [1]. They are blended with an ignition promoter in diesel engines whereas they, as high octane number fuels, can be used without major engine modifications in gasoline engines. DME is an excellent fuel for diesel engines [2]. It burns without formation of particulate matter and provides the diesel engine with a clean, low NOx and low cost fuel. DEE is also a diesel engine fuel with a very high cetane number [3].

In gasoline engines the fuel injection pressure is moderate so wear issues in the injection equipment are not significant challenges. In diesel engines the fuel injection pressure is of the order of 2000 bars or more so the ability of the fuel to lubricate the injection equipment is of significance. This property is named lubricity and is related to the ability of the fuel to protect the pump surfaces from wear in the boundary lubrication regime.

The lubricity of diesel fuel is predominately measured by the HFRR, the High Frequency Reciprocating Rig. The method is covered by both an ASTM [4] and an ISO standard [5]. Issues are encountered when volatile alternate fuels have to be tested: The HFRR can only operate at ambient pressure and 60C or 25C.

The Medium Frequency Pressurised Reciprocating Rig (MFPRR) has been developed to establish the lubricity of DME, pure or additised [6]. DME has a vapor pressure of six bars at 20 C so the whole test has to be enclosed.

The principle of the MFPRR is the same as in the HFRR. A steel ball is sled against a steel disk in the tested fuel with a load of 200g and a stroke of 1 mm in the HFRR (5 mm in the MFPRR) at a frequency of 50 Hz in the HFRR (10 Hz in the MFPRR). The duration

is 75 minutes. After the test the wear scar on the ball is evaluated. The major and minor axes of the wear scar are measured as shown in figure 1. The Wear Scar Diameter (WSD) is the average of the two axes.
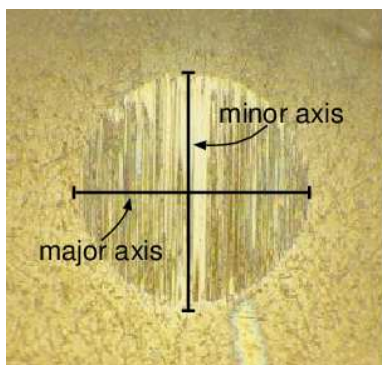

Figure 1: The wear scar on the ball is measured by averaging the major and the minor axes resulting in the wear scar diameter (WSD).

The currently used pass-fail limit for the HFRR WSD is 460 µm [5]. The repeatability is 80 µm at 60C for the HFRR [5] and 30 µm for the MFPRR [6] and this
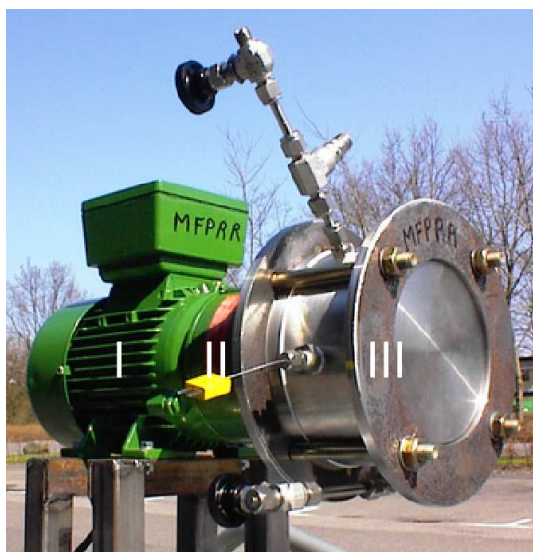
The 0utside of the MFPRR is shown in figure 2.

Figure 2: The outside of the MFPRR showing I) The electric motor II) The magnetic coupling III) The tank enclosing the rig.

The tank encloses the rig (figure 2 III) which is driven by the electric motor (figure 2 I) via a magnetic coupling (figure 2 II). The advantage of this construction is that no dynamic sealing is needed. Most elastomeric materials required for such seals react chemically with DME.

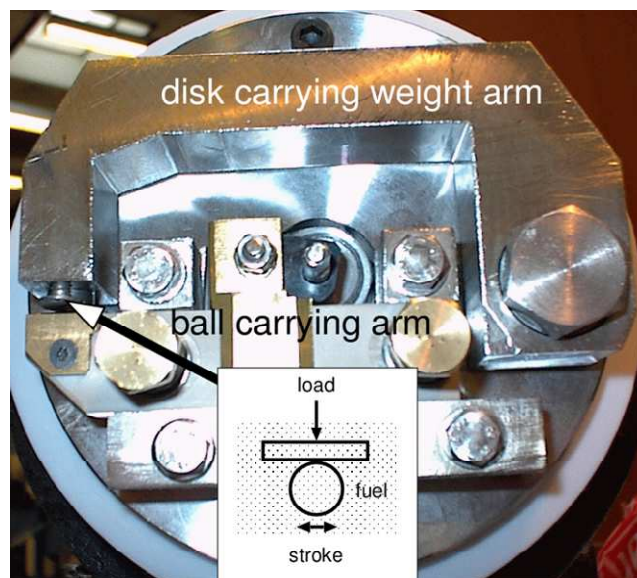The inside of the MFPRR is shown in figure 3.

Figure 3: The inside of the MFPRR showing the ball carrying arm driven by the shaft in the middle of the figure and the disk carrying arm providing the load between the ball and the disk. The insert shows a drawing of the disk on ball setup. .

The insert of figure 3 shows the disk on ball setup schematically. the ball is carried by the ball are which is driven by the shaft in the center of the rig. The disk arm carries the disk and provides the load between the test specimens. The tank is filled with fuel during the test.

The MFPRR has been used to establish the lubricity of DME [6]. The results are shown in figure 4. The lubricity of 99,99% pure DME is a WSD of 660 µm in the MFPRR. The HFRR is a more severe test than the MFPRR due to the lower stroke and higher frequency. In addition to this the HFRR is operated at 60C whereas the MFPRR uses 25C. The WSDs of the two methods cannot be compared though but the trend in the results is the same. To indicate the order of magnitude of the difference in the outcome of the methods, figure 4 shows the lubricity level of a typical diesel oil (404 µm in the HFRR, 172 µm in the MFPRR) and of kerosene (760 µm in the HFRR, 330 µm in the MFPRR). Three different lubricity additives have been used: Lubrizol 539N, a standard additive for diesel oil, Castor oil, a lubricant for two-stroke engines and rape seed oil methyl ester (RME) also called biodiesel. The trend in figure 4 is that very small amounts of additive increase the lubricity of DME significantly. The impact is more pronounced at small dosages until a lubricity plateau is reached. This plateau is dependent on the used additive and Lubrizol 539N provides the lubricity level comparable to that of

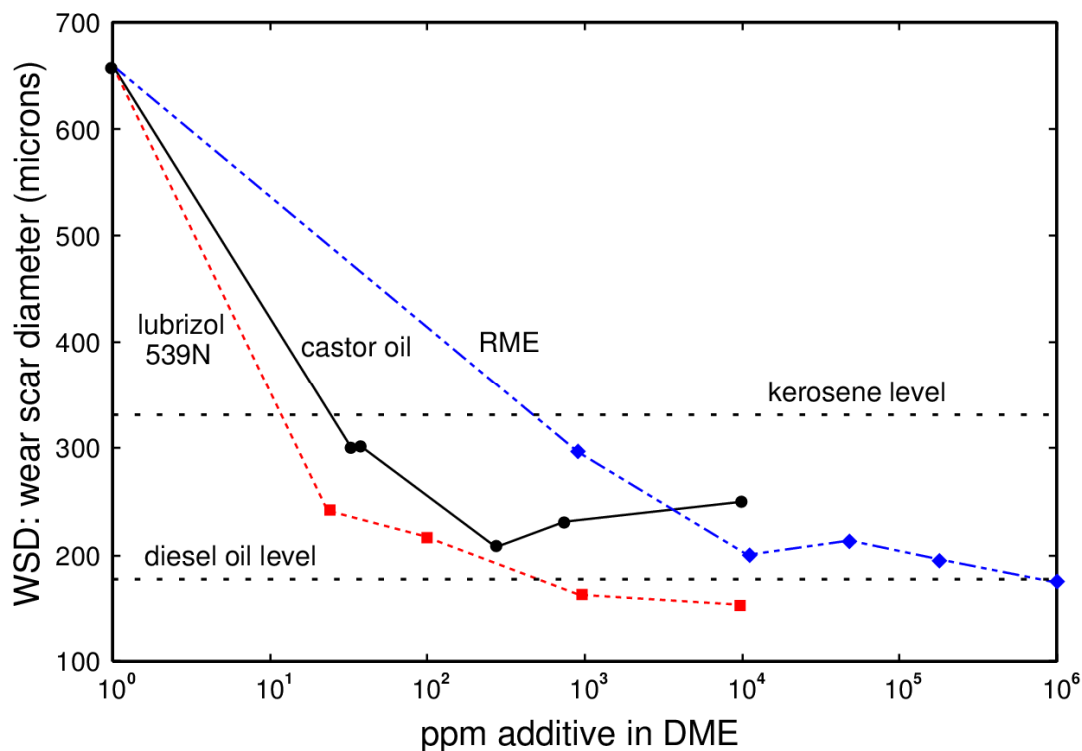diesel oil at a dosage of 1000 weight parts per million (ppm).

Figure 4: *The lubricity of DME expressed as the WSD as a function of the amount of additives. Results for Lubrizol 539N, castor oil and RME (Rape seed oil methyl ester) are shown. As references the lubricity of diesel oil and kerosene are indicated.*

2. METHODOLOGY AND SELECTED FLUIDS

OBATE™ consists of ether, alcohol and water. In the present study the lubricity of DME, DEE, methanol, ethanol and water is investigated. The fluids are "as pure as possible" to ensure that the MFPRR WSDs reflect the lubricity of the substances and not the effect of impurities. The DME is more than 99,99 % pure whereas the other fluids are of HPLC (Liquid for High Performance Liquid Chromatography) quality. The fluids are more than 99,9 % pure.

Some of the properties of the tested fuels are gathered in table 1. DME can only be tested in the MFPRR because of the low boiling point and even DEE is difficult to test in the HFRR even if the temperature is kept at 25C. The high cetane number of the ethers make them good diesel fuels whereas the high octane numbers of the alcohols make them suited for gasoline engines.

First the lubricity of the pure substances is measured at 25 C. Then water and/or lubricity additive is added. Finally the lubricity of the alcohols as a function of the water content is established.

Table 1: *A number of properties of the investigated fluids. The used water is also of HPLC quality.*

Property	DME	DEE	Methanol	Ethanol
Quality	>99,99%	*HPLC >99,9%	*HPLC >99,9%	*HPLC >99,9%
Formula	C2H6O	C4H10O	CH4O	C2H6O
Density (kg/m^3)	668	713	790	790
Viscosity (mm^2/s)	0,185 @ 25C	0,314 @ 25C	0,747 @20C	1,36 @25C
Boiling point (C)	-24,9	34,6	65	78
Cetane Number (-)	60	>125	Very low	Very low
Octane Number (-)	Very low	Very low	109	109

*HPLC: Liquid for High Performance Liquid Chromatography.

3. RESULTS AND DISCUSSION

The MFPRR for the pure substances and for the blends with or without water and lubricity additives are presented in table 2.

Table 2: *The lubricity of the investigated fuels with or without lubricity additive. The alcohols have also been blended with 25 percent water. The lubricity additive is identical or similar to the Lubrizol 539N used in figure 3*

Base fuel	Water content (%)	ppm lubricity additive	WSD (μm)
DME	-	0	660
DME	-	1000	162
DEE	-	0	614
DEE	-	5000	264
Methanol	-	0	450
Ethanol	-	0	403
Methanol	25	0	730
Ethanol	25	0	811
Methanol	25	5000	218
Ethanol	25	5000	264
Water	100	0	900

The used lubricity additive is identical or similar to the Lubrizol 539N from figure 4. The lubricities of the pure ethers are of the same order magnitude. This is not the case when a lubricity additive is used. At 5000 ppm the lubricity plateau is supposedly reached and a WSD of 264 μm is not impressively low. The effective additive response of DME is shown at 1000 ppm additive, WSD=162 μm, and the final plateau has not even been reached yet.

The lubricities of the pure alcohols are not that different either. It is surprising that the lubricity of ethanol with 25 % water is significantly lower than that of methanol also with 25 % water. The same is the truth when an additional 5000 ppm of lubricity fluid is added.

The fact that alcohols have higher lubricity than ethers is in good accordance with results found in the literature. Reference 7 presents the influence of different molecular species on the lubricity. One of the conclusions is that fluids with OH groups (alcohols) have higher lubricity than those with COC groups (ethers). This is consistent with the findings in the present work.

The main outcome of table 2 is that addition of water is affecting the lubricity of ethanol more than that of methanol. Therefore it is interesting to investigate the lubricity of alcohol-water blends more thoroughly.

It is important to point out that these alcohols are miscible with water in all concentrations. It means that all the bends are in one phase.
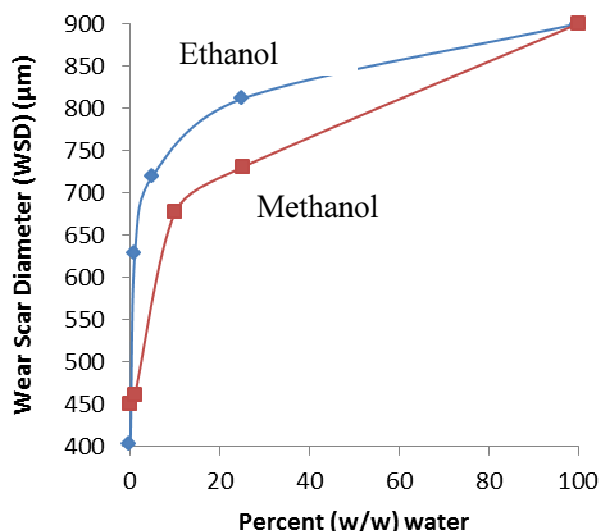

Figure 5: *The lubricity of alcohol-water blends expressed as the WSD as a function of the water content in percent w/w.*

Figure 5 shows the lubricity of the alcohols as a function of their water content. It is striking that already at five percent water the lubricity of ethanol is approaching that of water. At a dosage of one percent water the lubricity of methanol has not increased significantly.

At 25 % water the gap between the lubricities of methanol and ethanol is still significant and table 2 also shows that after blending with large amounts of additive the gap remains.

It is interesting observe the nature of the wear in the tests from figure 5. Figure 6 shows the wear scars on the balls from selected tests.
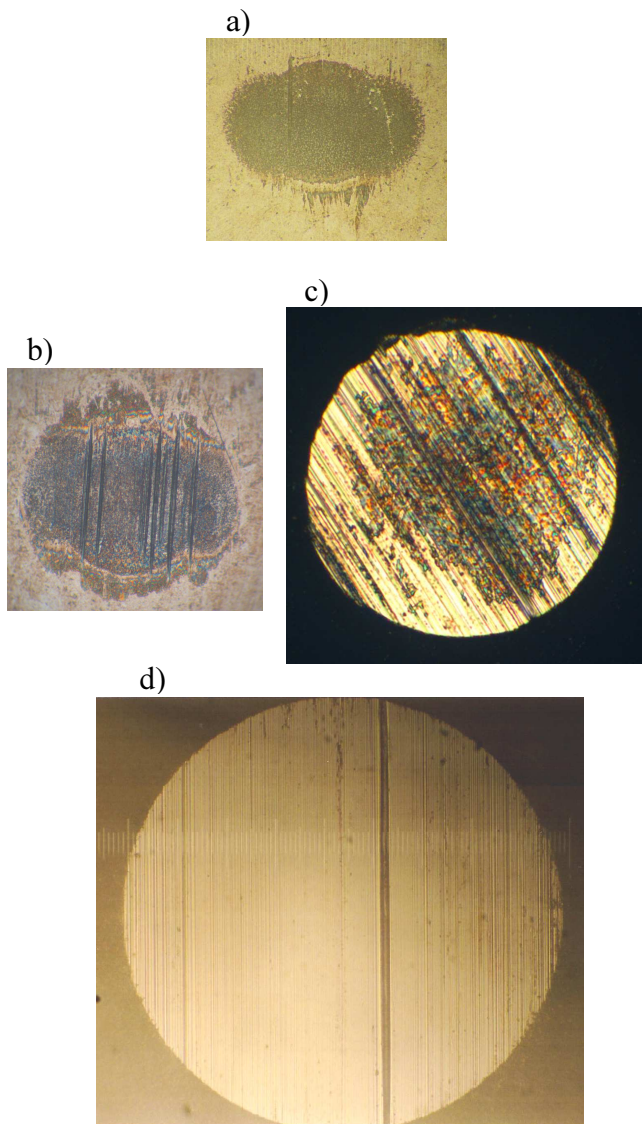
a)

c)

b)

d)

Figure 6: *The wear scars of a) Pure Ethanol WSD=403μm) b) Methanol with one percent water (WSD=461μm) c) Ethanol with one percent water (WSD=629μm) and d) Pure water (WSD=900μm)*

Figure 6a) shows the typical wear scar a pure alcohol. The shape is not circular and the ball is not actually worn, only scratched. The elliptic wear scar is due to more wear on the disk than on the ball. As the ball sinks into the disk the major axis is formed by sliding scratches whereas the minor axis is much smaller as it is formed by the impact of the ball with the disk at the ends of the wear track. Figure 6d) shows the wear scar of water which is huge. The form is circular and corresponds to the wear off of the top of the ball. The disk is practically not worn.

By observing figure 6b) it can be seen that the wear scar of Methanol with one percent water resembles that of pure alcohol, although it is a little larger. On the other hand the wear scar of ethanol with one percent water in figure 6c) is very similar in form to the water wear scar. It is significantly larger also.

In the present study there has been no optimisation with regards to the type of lubricity additive. Figure 6c) clearly shows traces of rust whereas these are not present in figure 6b). The main wear mechanism in the former case could then supposedly be corrosion but how the methanol can inhibit this cannot be explained.

It is thus predicted that ORBATE™E could be a tough lubricity challenge because it contains an ethanol-water blend. ORBATE™M could be more straight-forward as both the ether and the alcohol in this fuel are easier to improve with regards to the lubricity even if water is present.

4. CONCLUSIONS

OBATE™ fuels consist of ether, alcohol and water. The present study predicts that the DEE Ethanol based ORBATE™E is a more significant lubricity challenge than is the DME methanol based OBATE™M. This conclusion comes from two observations:

- DME lubricity responds more readably to lubricity additives than DEE
- When ethanol is blended with water the lubricity drops rapidly and reaches the level of water. On the contrary methanol keeps lubricating like an alcohol even if water is added in quite substantial amounts.

5. REFERENCES

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