Experimental investigations of the effect of biodiesel utilization on lubricating oil tribology in diesel engines

Article *in* Proceedings of the Institution of Mechanical Engineers Part D Journal of Automobile Engineering · May 2005

DOI: 10.1243/095440705X11239

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Experimental investigations of the effect of biodiesel utilization on lubricating oil tribology in diesel engines

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The manuscript was received on 27 August 2004 and was accepted after revision for publication on 13 January 2005.

DOI: 10.1243/095440705X11239

Abstract: Biodiesel is an alternative fuel derived from vegetable oils by modifying their molecular structure through a transesterification process. Linseed oil methyl ester (LOME) was prepared using methanol in the presence of potassium hydroxide as a catalyst. The use of LOME in compression ignition engines was found to develop a very compatible engine-fuel system with lower emission characteristics. Two identical engines were subjected to long-term endurance tests, fuelled by an optimum biodiesel blend (20 per cent LOME) and diesel oil, respectively.

Various tribological studies on lubricating oil samples drawn at regular intervals for both engines were conducted in order to correlate the comparative performance of the two fuels and the effect of fuel chemistry on lubricating oil performance and life. A number of tests were conducted in order to evaluate the comparative performances of the two fuels such as density measurement, viscosity measurements, flashpoint determination, moisture content determination, pentane and benzene insolubles, thin layer chromatography, differential scanning calorimetry, etc. All these tests were used for an indirect interpretation of the comparative performance of these fuels. The performance of biodiesel fuels is found to be superior to that of diesel oil and the lubricating oil life is found to increase while operating the engine on biodiesel.

Keywords: biodiesel, long-term endurance test, oil tribology, viscosity, flashpoint, moisture content, insoluble, thin layer chromatograhy, additive depletion, differential scanning calorimetry

1 INTRODUCTION

The Kyoto Protocol stressed the importance of a cleaner environment, and the sustainable development of our natural resources in this technologically galloping era goes hand-in-hand with this. Sustainable development, synonymous with the directive ‘proceed with caution’, in a broader sense implies the utilization of present resources in a proficient manner. Vegetable oils are an attractive and promising alternative to diesel oil since they are renewable and can be produced easily in rural areas, where there is an acute demand for energy. The oil supply shock in the 1970s triggered developments in the field of biodiesel. The strongest impulse was given by the crisis in the supply of mineral oil as the major source of energy in the 1970s, and again by the Gulf war in 1991. In modern times also, petroleum prices have risen to new levels. The production–demand gap of fossil oils is declining worldwide and countries that are highly dependent on huge imports of fossil oil are facing an increasing risk in the security of energy supply.

Vegetable oils have approximately 90 per cent of the heat content of diesel fuel. The combustion-related properties of vegetable oils are somewhat similar to diesel. Vegetable oils, or their blends with diesel, pose various long-term problems in compression ignition engines, for example: poor atomization of fuel, ring-sticking, injector-coking and deposits, injector pump failure, lubricating oil dilution, crank-case polymerization, etc. The properties responsible for these problems are the high-viscosity, low volatility, and polyunsaturated characteristics of vegetable oils [**1**, **2**]. Since viscosity is one of the key properties in making a fuel usable in diesel engines, the aim then becomes not only to reduce the viscosity but also to minimize other undesirable properties of vegetable oils. This includes reducing the carbon chain length, increasing volatility, and reducing the unsaturation of vegetable oil molecules [**1**]. Thus, it has to be converted to a more engine-friendly fuel called biodiesel (vegetable oil esters).

A research study at the University of Idaho shows that biodiesel degraded up to four times faster than petroleum diesel and a blend (50 per cent diesel and 50 per cent biodiesel) degraded in one-third of the time compared with petroleum-based diesel fuel [**4**]. In addition, biodiesel offers lower exhaust emissions than diesel fuel. With 10–20 per cent lower CO, particulate matter, and unburned hydrocarbon emissions, biodiesel proves to be a ‘cleaner’ fuel. Marginally higher NO_x emissions (2–4 per cent), coupled with decreased engine exhaust temperatures have led researchers to believe that methyl esters, acting as cetane improvers, result in a reduced ignition delay time, and they thus effectively advance the injection timing. One method of dealing with increased biodiesel NO_x emissions is to delay the injection timing of the engine. Another option that is being investigated at the National Center for Agricultural Utilization Research (NCAUR), Illinois, USA is the use of fuel additives to control NO_x emissions. However using an oxidation catalyst or catalytic converter reduces emissions by more than 40 per cent for total hydrocarbons, 30 per cent for particulates, and 20 per cent for CO [**1**]. A minor inconvenience of marginally higher NO_x should not detract from the numerous advantages that biodiesel offers [**3**, **2**].

Transesterification is a chemical reaction in which triglycerides present in vegetable oils react with three molecules of primary alcohol such as methanol and yield three molecules of esters (biodiesel). It is a reversible reaction, which is either acid or alkali-catalyzed, and involves stepwise conversions of triglycerides to diglycerides to monoglycerides to glycerol [**5**]. The reaction is carried out at 65–70 °C for approximately an hour, followed by gravity separation of glycerol from esters. Since transesterification is a reversible reaction, an excess of alcohol is required to force the reaction towards completion. Alkaline catalysts have the advantage of being less corrosive to industrial equipment than acid catalysts. Glycerol is a valuable by-product, which is used in pharmaceuticals, cosmetics, toothpaste, and many other commercial products. Biodiesel is often blended with petroleum diesel to offset its high production cost [**1**, **2**, **6–8**].

In an engine, the cost of the lubricating oil alone is approximately 6–7 per cent of the overall operating costs. Hence, it becomes imperative to examine critically the condition of the lubricating oil, and its compatibility with the fuel being used [**9**]. In addition to the length of service since the last oil change, the overall oil condition and oil degradation rate depends on other factors such as engine condition, driving environment, rates of oil consumption and addition, depletion of additives such as zinc-di-alkyl-di-thio-phosphate (ZDDP), etc. [**10–19**].

2 EXPERIMENTAL SET-UP

Two similar engines were selected for this study. These were compact, single-cylinder, water-cooled, portable diesel engines of 4 kW capacity coupled with AC generators. The inlet valve opens at 4.5° before top dead centre (BTDC) and closes at 35.5° after bottom dead centre (ABDC). The exhaust valve opens at 35.5° before bottom dead centre (BBDC) and closes at 4.5° after top dead centre (ATDC). Technical specifications of the engines are given in Table 1. The engines were provided with arrangements that permitted a wide variation of various operating parameters.

The proportion of esters in the biodiesel blend was optimized using the performance and emission test conducted on several biodiesel blends and a 20 per cent biodiesel blend was found to be the optimum [**4**]. A long-term endurance test specified by Indian Standards Code (IS: 10000, 1980, Methods of tests for internal combustion engines) was carried out with this optimized blend. In the long-term endurance test, the effect of fuel chemistry of biodiesel on various engine parts vis-à-vis mineral diesel was studied. For this purpose, these two similar engines were subjected to similar loading cycles and operating conditions. The engines were dismantled, re-assembled, and mounted on the test bed after recording the dimensions of vital engine parts. The engines were run for 32 cycles (each of 16 h continuous running) at rated speed. The test cycle is specified in Table 2.

At the end of each test cycle, minor engine adjustments were made. The lubricating oil samples were collected from each engine after every 128 h interval for conducting various tribological studies. The samples were drawn according to standard sampling procedure [**1**, **20**].

Table 1 Technical specifications of test engines

Manufacturer	Perry Engines Ltd, India
Bore	87.5 mm
Stroke	110 mm
Displacement	661.7 cm^3
Rated speed	1500 r/min
Maximum speed	2000 r/min
Minimum idling speed	750 r/min
Compression ratio	17 : 1

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Table 2 Test cycle for long-term endurance test

Load (% of rated load)	Running time (h)
100	4 (including warm-up for 0.5 h)
50	4
110	1
No load (idling)	0.5
100	3
50	3.5

3 TRIBOLOGICAL STUDIES ON LUBRICATING OIL

Prior to adopting any alternative fuel for regular use in conventional engines, it is essential that the tribological investigations relating to lubricating oil be conducted. Various lubricating oil tribology studies can be conducted to assess the effect of different fuels on an engine's health. A number of factors affect lubricating oil performance: oil thickening, depletion of wear protection additives, and deposit control additives are of primary concern in high-temperature, high-load conditions. Oil thinning, depletion of corrosion protection additives, and low-temperature sludge formation are of concern primarily in short engine runs [**14**].

The following tests were selected in this study to assess the condition of the lubricating oil samples drawn from diesel- and biodiesel-fuelled engines: density, kinematic viscosity, ash content, water content, flashpoint, pentane and benzene insolubles, Fourier transform infrared (FTIR) spectroscopy, sealed pan differential scanning calorimetry (SPDSC), thin layer chromatography (TLC), atomic absorption spectroscopy (AAS), and direct-reading (DR) ferrography. These exhaustive tests provide valuable information on the effect of biodiesel on the lubricating oil vis-à-vis diesel.

The oil cannot be discarded or declared fit for further use based on a single test. The oil performance is generally evaluated on the basis of various analytical techniques. TLC was carried out to evaluate the residual concentration of ZDDP in the lubricating oil samples. ZDDP is a very important wear protection additive in lubricating oil. The determination of metals in lubricating oils has always been a challenge in analytical chemistry. Metals such as Ba, Ca, Mg, etc. are added to the lubricating oil in the form of organo-metallic additives to improve colour, pour point, viscosity, antiwear, antifriction, antifoaming, oxidation, corrosion inhibition properties, and oil performance [**15**, **16**]. In addition, metals such as Fe, AI, Cu, Zn, Co, and Ni become accumulated in oil in the form of wear debris. Therefore, determination of the metal content in used oils is important to identify possible defective functioning areas of the oil-lubricated equipment and to schedule maintenance accordingly. Modern techniques such as inductively coupled plasma (ICP), optical emission spectrometry, and AAS have been widely used for metal analysis [**16**, **17**]. The differential scanning calorimetry (DSC) technique determines the concentration of degradation products in lubricating oils such as oxidation and nitro-oxidation products, additive depletion, and contaminations [**22**]. The SPDSC technique is the most recent and has been applied for evaluation of residual useful life (RUL) of oil under induced thermo-oxidative stresses in the laboratory [**18**]. Oxidation and combustion of lubricating oils often result in the formation of insoluble deposits on the metal surfaces. Accumulation of sludge and varnish deposits on engine parts causes poor lubrication and increased wear, therefore, the deposit-forming tendency of lubricating oil is one of the major concerns in oil evaluation [**19**].

4 RESULTS OF ENGINE TESTS AND TRIBOLOGICAL STUDIES ON LUBRICATING OIL

The two engines were operated for 512 h on two different fuels namely diesel and 20 per cent biodiesel blend. During this long-term endurance test on engines, the extent of durability problems such as fuel filter plugging, injector coking, carbon deposits in combustion chamber, ring sticking, and contamination of lubricating oils were found to be substantially lower for the biodiesel-fuelled engine compared with the diesel-fuelled engine. The fuel handling system also operated normally on biodiesel blend. This suggests that the operational and durability problems associated with vegetable oil as fuel were not observed with biodiesel [**16**]. The detailed results of engine tests are available in published literature [**2**, **16**].

The lubricating oil samples were drawn from the two engines and analysed. Experimental results of several lubricating oil tribology tests conducted are discussed below.

4.1 Density

Density measurements are important since they provide information on the addition of wear metals and fuel dilution in lubricating oil. The density of lubricating oil from both the engines shows an increasing trend with usage. The density increased

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faster in the initial phase of engine operation. The rate of increase in density decreased after 128 h. It can be observed from Fig. 1 that the density of lubricating oil from the diesel-fuelled engine increased at a faster rate, which may be due to following reasons.

1. Wear debris addition in lubricating oil from the biodiesel-fuelled engine may be lower.
2. Fuel dilution in the case of the biodiesel-fuelled engine may be lower as biodiesel may be helping reduce blow-by.
3. Addition of moisture to lubricating oil from blow-by gases may be lower in case of biodiesel-fuelled engine.

These possible reasons suggest that blending of biodiesel to mineral diesel improved the density change pattern in the lubricating oil. The most important observation of this study was that lubricating oil drawn from the biodiesel-fuelled engine had a lower deterioration in density throughout the engine operation thereby indicating lower wear of vital engine components, lower fuel dilution, and moisture addition, which is further investigated by different tests.

4.2 Ash content

Ash content reflects non-carbonaceous material in the lubricating oil since carbonaceous materials such as oil, soot, fuel, and non-metallic parts of organo-metallic additives are converted into CO_2 after thermal decomposition. Ash content mainly indicates metallic wear debris and abrasive foreign particles like dust entering the system. Since both engines were operated under similar conditions, the contribution of foreign particles was assumed to be similar hence variation in ash content of lubricating oils drawn from the two engines primarily reflected wear debris (Fig. 2). It was observed that the ash content in the lubricating oil drawn from the biodiesel-fuelled engine was approximately 15 per cent lower than that of the diesel-fuelled engine. Figure 2

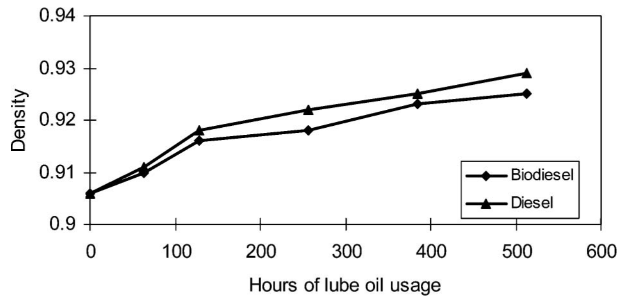

Fig. 1 Density versus hours of lubricating oil usage

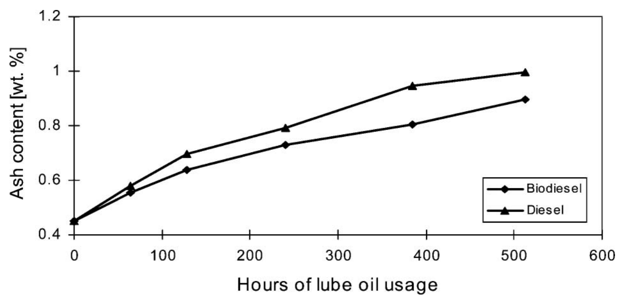

Fig. 2 Ash content versus hours of lubricating oil usage

suggests that the biodiesel-fuelled engine produced a lower amount of metallic wear debris. This was also confirmed by AAS analysis of lubricating oils drawn from the two engines [**16**].

4.3 Viscosity

Any change in viscosity of the lubricating oil is undesirable in an engine as it affects the lubrication. In fact, the criterion for replacing lubricating oil states 'change the lubricating oil if viscosity increases by 20 per cent or more, or decreases by 10 per cent or more' [**20**]. The viscosity of lubricating oil may increase or decrease with usage. Inadequate oil viscosity affects the lubricating oil film thickness separating the metallic parts and load-bearing capacity leading to low oil pressure, poor oil efficiency, and excessive wear of mating parts, bearings, and other moving components.

Two factors are mainly responsible for lubricating oil viscosity changes in opposite directions. Formation of resinous products because of oil oxidation, evaporation of lighter fractions, depletion of antiwear additives, and contamination by an insoluble tend to increase the oil viscosity while moisture addition, fuel dilution, and shearing of the viscosity index improvers tend to reduce oil viscosity. The extent of dominance of both mechanisms however differs from system to system. The viscosity of all lubricating oil samples was evaluated at 40 °C and 100 °C using a Setavis kinematic viscometer (Figs 3 and 4). An

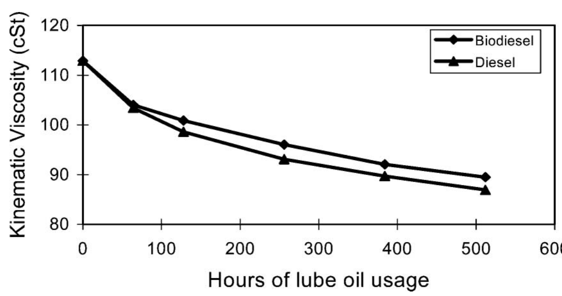

Fig. 3 Kinematic viscosity at 40 °C versus hours of lubricating oil usage

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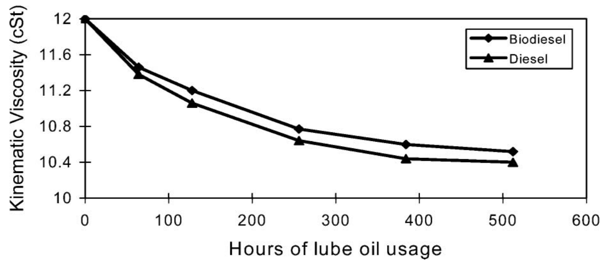

Fig. 4 Kinematic viscosity at 100 °C versus hours of lubricating oil usage

important observation was that a reduction in the viscosity of lubricating oil drawn from biodiesel-fuelled engine is lower compared with diesel-fuelled engine. This may be possibly due to lower fuel dilution and moisture addition. Fuel dilution is a consequence of clearance between the piston rings and cylinder liner and the wear of the piston rings. Since biodiesel has inherent lubrication properties, it helps in protecting the piston rings from wear more effectively [**21**]. Relatively higher viscosity of biodiesel helps in reducing blow-by losses and fuel dilution of lubricating oil.

The viscosity behaviour, however, cannot be neglected. Rate of change of viscosity is also controlled by oil oxidation. It is also possible that biodiesel, which gets in to lubricating oil through fuel dilution, might have accelerated the oxidation rate of base-stock leading to slightly higher viscosity. Hence, the decrease in viscosity due to fuel dilution could have slowed down due to base-stock oxidation. This hypothesis was supported by FTIR studies, which showed higher oxidation of lubricating oil base-stock for the biodiesel-fuelled engine [**2**].

4.4 Flashpoint

The flashpoint temperature of all the lubricating oil samples was evaluated using the Pensky–Martens apparatus. On heating, the lubricating oil molecules experience van der Waal's forces. The higher the van der Waal's forces, the higher the energy required for vaporizing will be and the higher the flashpoint. Fuel dilution of the lubricating oil is undesirable because it will reduce the van der Waal's forces to a greater extent, thus lowering the flashpoint.

As observed in Fig. 5, the flashpoint of lubricating oils from both the engines decreased with usage. Lubricating oil from the biodiesel-fuelled engine showed approximately 5 per cent lower decrease in flashpoint compared with the diesel-fuelled engine. This suggested that the fuel dilution of the lubricating oil was higher for the diesel-fuelled engine. This is similar to the observation made in earlier

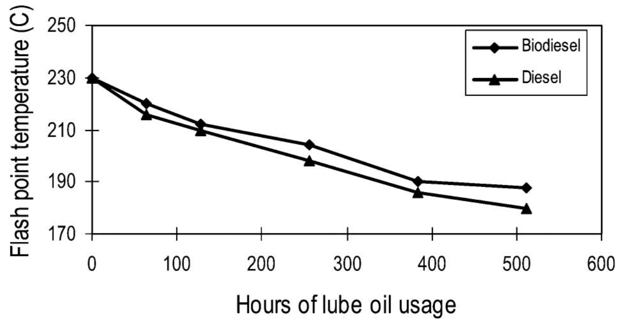

Fig. 5 Flash point versus hours of lubricating oil usage

tests. The flashpoint of mineral diesel oil (76 °C) is lower than for the biodiesel blend (128 °C). Hence, dilution of the lubricating oil with a fuel of lower flashpoint should reduce the flashpoint of the lubricating oil to a greater extent.

4.5 Moisture content

Traces of moisture in lubricating oil can increase corrosion inside an engine. Water traces may also cause 'additive drop out', i.e. precipitation of additives from the lubricating oil. The presence of water traces in the lubricating oil may also indicate excessive fuel dilution, coolant leakage, and short trip driving conditions. A Mettler DL18 Karl Fischer titration unit (ASTM D 1744) was used to determine the moisture content in the lubricating oil. The experimental results are shown in Fig. 6.

Approximately 15 per cent lower moisture content is observed in the lubricating oil from the biodiesel-fuelled system. The initial rate of absorption of moisture was quite high, which stabilized after 400 h. The lower moisture content in the lubricating oil from the biodiesel-fuelled engine may be because of additional lubricity exhibited by the biodiesel, resulting in improved sealing of the piston ring–liner interface. Improved engine sealing will give lower engine blow-by and thus a lower amount of moisture will condense in the lubricating oil in the crank case.

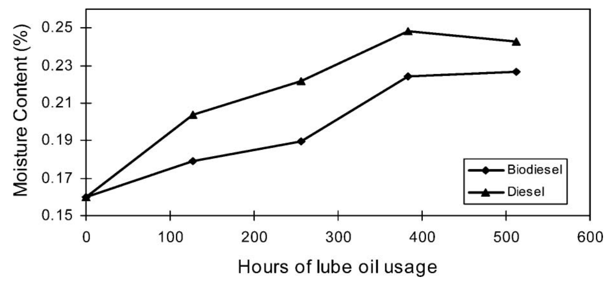

Fig. 6 Moisture content versus hours of lubricating oil usage

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4.6 Pentane and benzene insolubles

Used lubricating oil generally contains the following suspended contaminations:

(a) oil-soluble resinous material formed as a result of degradation of oil, additives, or both;
(b) fuel carbon or highly carbonized substances;
(c) corrosion and wear particles originated from the engine;
(d) dust particles entering from the environment.

Mainly two types of methods are used for insoluble quantification namely pentane and benzene insoluble. Both the solvents have different chemical structures and hence they have preferential solubility for various materials. Pentane is aliphatic in nature and dissolves only lubricating oils. The resinous materials, which were otherwise soluble in oil, are thrown away as insoluble. The pentane insoluble contains all the ingredients as in (a), (b), (c), and (d). Benzene is aromatic and dissolves resinous material along with lubricating oil, hence the benzene insoluble contains ingredients as in (b), (c), and (d). The weight of insolubles in benzene is lower than that of pentane. The difference between the pentane and benzene insolubles indicates the extent of oil oxidation. The higher the difference, the higher is the oil oxidation, and the lower the residual useful life of the lubricating oil. The method followed for insoluble determination in this study is described in ASTM D893-63. These tests were conducted using a Remi oil centrifuge, centrifuge tubes with corks, solvents, and balance.

The pentane insoluble as a function of lubricating oil usage is shown in Fig. 7. It can be observed that lubricating oil drawn from a biodiesel-fuelled engine indicated approximately 40 per cent lower insoluble. This indicates a comparatively better lubricating oil condition of the biodiesel-fuelled engine. The lubricating oil from the biodiesel-fuelled engine is prone to higher oxidation because of the oxidative properties of biodiesel. In spite of higher oxidation products formed in the biodiesel-fuelled engine, pentane insolubles are in larger quantities in the lubricating oil drawn from diesel-fuelled engine. The probable reason for this is that diesel does not have the inherent lubricating properties of biodiesel and the depletion of antiwear and extreme pressure additives is higher in a diesel-fuelled engine. It has also been reported [**14**] that excessive moisture content in the lubricating oil may be responsible for 'wash out' of these additives. This observation is also confirmed during the experiments conducted for determination of moisture content, described earlier.

Results on the benzene insoluble of lubricating oils are shown in Fig. 8. In the lubricating oil drawn from the biodiesel-fuelled engine, the benzene insoluble increased with a slow and steady rate, while in the case lubricating oil drawn from diesel-fuelled engine, it increased excessively beyond 300 h. The obvious reason for this behaviour is an excessive increase in wear of vital components of the diesel-fuelled engine. Lower wear of vital components of the biodiesel-fuelled engine reflects inherent lubricity properties of biodiesel. These findings are substantiated by the physical dimensioning of vital engine components for wear, wear metal analysis of lubricating oil, and ash content measurements [**16**].

4.7 Thin layer chromatography (TLC)

TLC is an effective technique for estimating additive depletion such as ZDDP with the usage of lubricating oil. The additive depletion in the lubricating oils drawn from diesel- and biodiesel-fuelled engine is compared. ZDDP is a very popular multifunctional additive for lubricating oils, which combines antiwear, anti-oxidation, detergent, and corrosion-inhibiting properties. Tests were conducted using two different revealing reagents, namely palladium chloride ($PdCl_2$) and rhodamine B. The corresponding chromatograms for lubricating oils having varying quantities

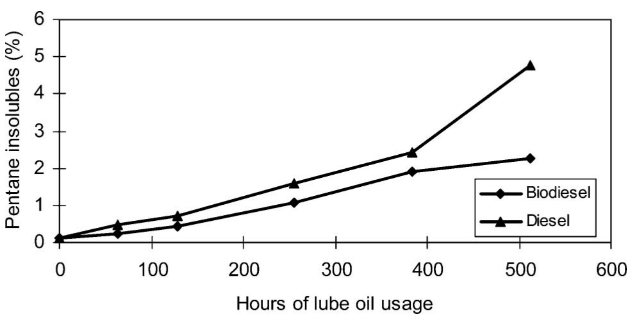

Fig. 7 Pentane insoluble versus hours of lubricating oil usage

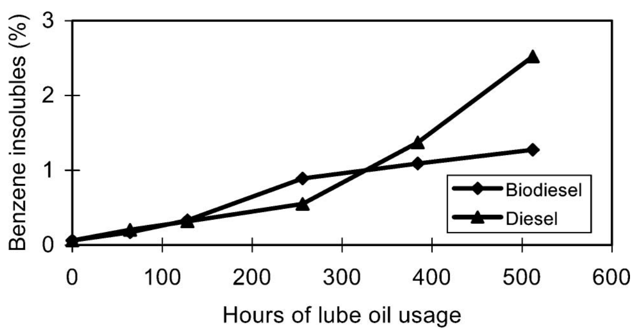

Fig. 8 Benzene insoluble versus hours of lubricating oil usage

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of ZDDP using these revealing agents are shown in Figs 9 and 10, respectively. The chromatogram based on $PdCl_2$ shows an increased intensity of brown coloured spots with an increase in ZDDP concentration. Similarly, the chromatogram based on rhodamine B also showed an increasing intensity of mauve-coloured spots with an increase in concentration of ZDDP. Both chromatograms confirm that the intensity of spots can reliably be correlated with the quantity of ZDDP remaining in the lubricating oil.

The $PdCl_2$ chromatograms developed for lubricating oils drawn from diesel and biodiesel-fuelled engines are shown in Figs 11 and 12, respectively.

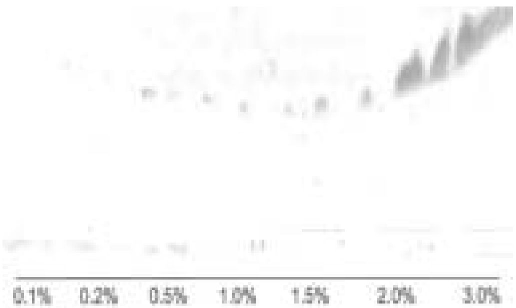

Fig. 9 TLC of lubricating oils having various concentrations of ZDDP using $PdCl_2$ as revealing agent

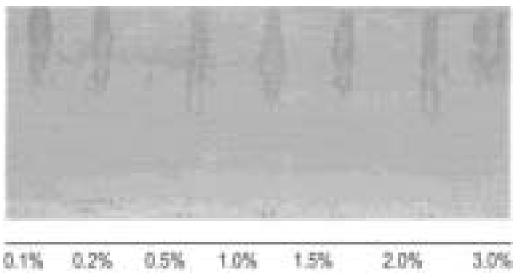

Fig. 10 TLC of lubricating oils having various concentrations of ZDDP using rhodamine-B as revealing agent

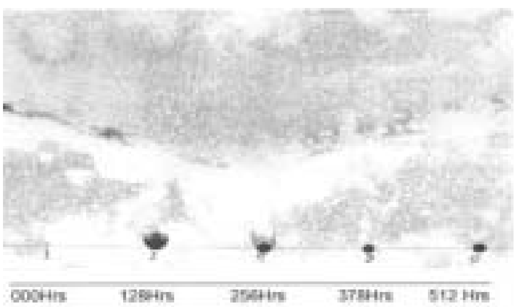

Fig. 11 TLC of lubricating oils from diesel engine using $PdCl_2$ as revealing agent

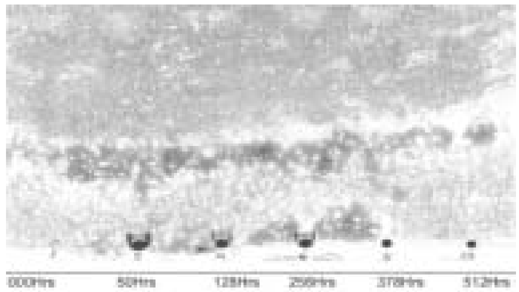

Fig. 12 TLC of lubricating oils from biodiesel-fuelled engine using $PdCl_2$ as revealing agent

The chromatograms clearly indicated that, with increasing usage, the intensity of brown spots on a puff-coloured background decreased indicating a continuous depletion of ZDDP. It is also observed that ZDDP did not deplete completely in the lubricating oil drawn from the biodiesel-fuelled engine. On the contrary, the lubricating oil drawn from the diesel-fuelled engine did not show a comparable amount of ZDDP beyond 378 h. Even in case of rhodamine B chromatograms (Figs 13 and 14), similar results were observed, which confirmed the faster rate of depletion of ZDDP in the lubricating oil from the diesel-fuelled engine. These results reinforce the findings of earlier tests, and suggest that wear is significantly lower in the biodiesel-fuelled engine.

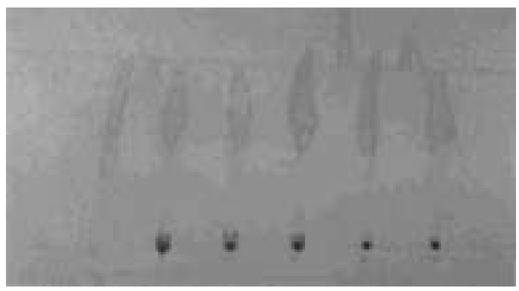

Fig. 13 TLC of lubricating oils from diesel-fuelled engine using rhodamine-B as revealing agent

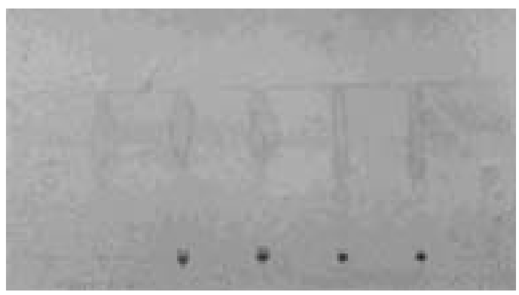

Fig. 14 TLC of lubricating oils from biodiesel-fuelled engine using rhodamine-B as revealing agent

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4.8 Analytical ferrography

During the life cycle of an engine, microscopic particles wear out from various moving parts. The particle size distribution, number, and the shape can give considerable information about the condition of the part they originate from, and the form of wear and wear mechanisms. Wear particle analyses of the lubricating oil can, therefore, be used as a tool for monitoring not only the health of engine oil but also moving parts.

A DR ferrograph (Fox Boro/Trans-Sonics Inc.) was used for the present evaluation. A bichrome microscope was used for particle analyses. The origin of the particles could be inferred from the composition of these particles, e.g. indications of bronze, copper, or a special type of steel may be traced to specific bearings. It can be observed from the ferrograms shown in Figs 15 to 18 that the number density of ferrous particles increased with usage of lubricating oil. In lubricating oil drawn from the biodiesel-fuelled engine, the size of the wear debris is significantly smaller compared with the diesel-fuelled engine. This might be a reflection of inherent lubricity of biodiesel, which prevents wearing out of components to some extent. In the diesel-fuelled engine, the fuel does not have such special inherent lubricity properties, hence the wear debris is larger in size. Bigger wear debris acts like abrasive particles and undergoes three body wear, damaging the surfaces further resulting in a higher wear of components with usage.

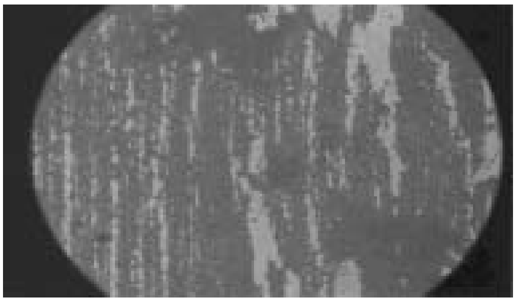

Fig. 15 Ferrogram showing wear debris in lubricating oil from diesel engine after 128 h of usage

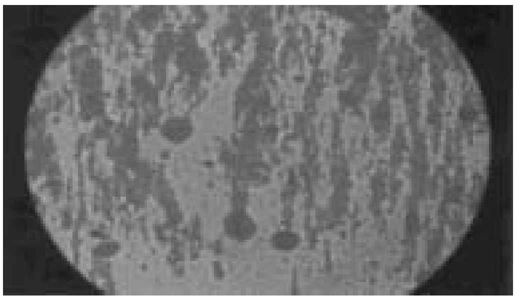

Fig. 16 Ferrogram showing wear debris in lubricating oil from diesel engine after 128 h of usage

Fig. 17 Ferrogram showing wear debris in lubricating oil from diesel engine after 512 h of usage

Fig. 18 Ferrogram showing wear debris in lubricating oil from biodiesel engine after 512 h of usage

4.9 Sealed pan differential scanning calorimetry (SPDSC)

The DSC technique involves raising or lowering the temperature of a sample and reference at a constant rate. By measuring the rate of heat flow extracted or supplied to the sample as a result of exothermic or endothermic reactions, the thermal properties of the sample can be determined. DSC has been applied to assess the stability of a range of lubricants and antioxidant packages. Good correlation has been observed for characterizing the deposit-forming tendencies of diesel with engine performance. DSC has also been used to propose a kinetics model for tri-acetylphosphate oxidation, and predict optimum additive systems and concentrations for inhibiting oxidation in lubricating oils, aluminium greases, and lithium greases. The use of a pressurized environment has also been recognized as essential to suppress the evaporation of the lubricant. This has been achieved by modification of the existing DSC chamber to incorporate high pressures, use of a separate pressurized cell, and use of an oxygen-purged sealed pan

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or capsule. The SPDSC is the least developed method yet, which has advantages of lower instrumental cost and easier operational technique in comparison to its high-pressure counterparts [**22**, **23**].

In the present study, SPDSC is used to measure the oxidation induction time (T_i) and oxidation stability of lubricating oils drawn from diesel and biodiesel-fuelled engines. Generally, the shorter the induction time, the lower is the thermal stability of lubricating oil. DSC induction times are reduced by the presence of fuel in the lubricating oil and are influenced by the temperature at which the test is conducted. The tests were conducted on Du-Pont equipment. Aluminium pans were filled with 20 μL of lubricating oil samples and sealed while pouring oxygen. Test parameters selected were as follows.

Start temperature = 140 °C

Ramp rate = 10 °C/min up to 140 °C and then 5 °C/min up to 300 °C

The thermograms for the lubricating oils (after 256 h) from the two engines, i.e. diesel- and biodiesel-fuelled engines were compared with the thermograms of fresh lubricating oil (Figs 19–21). A graph is drawn between the initiation temperatures of oxidation peaks in these thermograms versus hours of lubricating oil usage, Fig. 22. This curve reveals the destabilization route of the lubricating oils with usage for both engines. Figure 22 suggests that the oxidation stability of lubricating oil from the biodiesel-fuelled engine is lower than that of diesel-fuelled engine. The presence of oxygen in the molecular structure of biodiesel might be responsible for its lower oxidation stability.

The summary of various tribological tests for the lubricating oils drawn for diesel and biodiesel-fuelled engines was prepared (Table 3). It is interesting to

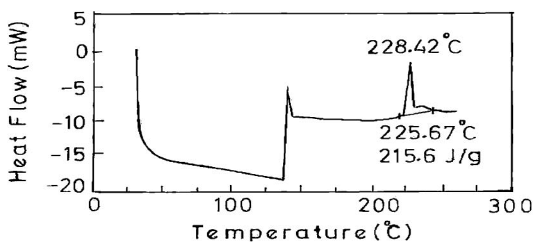

Fig. 19 SPDSC thermogram of fresh lubricating oil

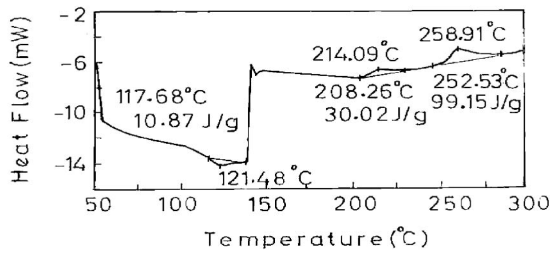

Fig. 20 SPDSC thermogram of lubricating oil from diesel-fuelled engine after 256 h of usage

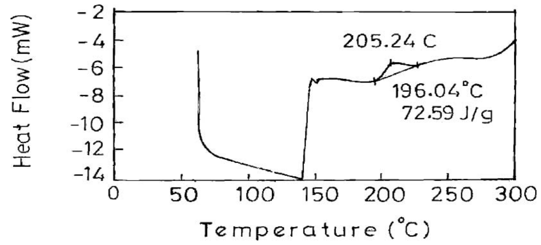

Fig. 21 SPDSC thermogram of lubricating oil from biodiesel-fuelled engine after 256 h of usage

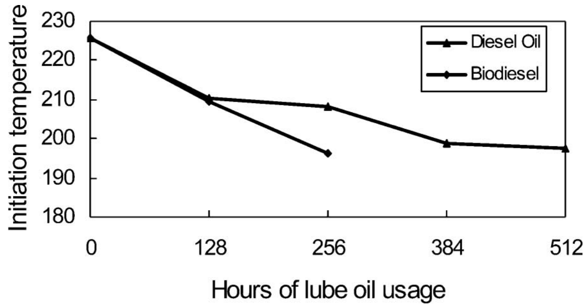

Fig. 22 Curve between initiation temperature and hours of lubricating oil usage

Table 3 Tribological investigations summary

Property	Trend with usage (diesel)	Trend with usage (biodiesel)	Comparison of biodiesel with diesel
Density	↑	↑	20% lower
Ash content	↑	↑	25% lower
Viscosity at 40 °C	↓	↓	17% lower
Viscosity at 100 °C	↓	↓	10% lower
Flashpoint	↓	↓	15% lower
Moisture content	↑	↑	30% lower
Pentane insoluble	↑	↑	60% lower
Benzene insoluble	↑	↑	50% lower
SPDSC (oxidation stability)	↓	↓	Slightly higher

note that the performance of biodiesel was better in almost all the aspects relating to lubricating oil tribology. However, it is suggested that some changes in the composition of lubricating oil (additive package) may be required to suppress undesirable properties of this new fuel for a dedicated biodiesel-fuelled engine. The lubricating oil's improved tribological behaviour is a consequence of improved fuel combustion and role played by the traces of biodiesel mixed with the lubricating oil through fuel dilution and blow-by. These traces affect the interaction of the engine surfaces and lubricating oil because of the superior lubricity properties. From this detailed study, it can be concluded that biodiesel is a strong candidate for partial replacement of mineral-based diesel fuels and it has a comparable engine performance, an almost similar exhaust emission spectra, and better lubricating oil tribology compared with mineral-based diesel fuel.

5 CONCLUSIONS

Based on exhaustive engine and tribological investigations of the lubricating oil, it can be concluded that biodiesel can overcome most of the operational and durability concerns existing with vegetable oils such as fuel filter plugging, injector coking, carbon deposits in combustion chamber, ring sticking, contamination of lubricating oils, etc. A long-term endurance test proved that biodiesel can be successfully used for partially substituting mineral diesel. This increases the likelihood of biodiesel being adopted as an alternative fuel for the existing conventional diesel engines without any major modifications in the engine hardware.

Comparative studies on various samples of lubricating oil indicated that the density increased with the usage of lubricating oil. It was found that the amount of various possible contaminants such as wear debris, soot, resinous compounds, oxidation products, and moisture content was lower in the case of lubricating oil drawn from the biodiesel-fuelled engine compared with the diesel-fuelled engine. The improved performance of biodiesel-fuelled system is possibly attributed to the inherent lubricity of biodiesel, resulting in lower wear of vital moving components. Ash content, which mainly represents wear debris, is found to be lower in the lubricating oil from the biodiesel-fuelled engine. Viscosity of the lubricating oil decreased with usage mainly due to fuel dilution. The extent of fuel dilution was lower for the lubricating oil from the biodiesel-fuelled engine. Flashpoint studies also supported improved performance of the biodiesel-fuelled system. Pentane and benzene insolubles reflected the extent of wear of moving parts, oil oxidation, and additive depletion and these were lower for the lubricating oil from the biodiesel-fuelled engine. The TLC technique reflected lower ZDDP depletion in the lubricating oil from the biodiesel-fuelled engine. Ferrograms revealed a lower number density and smaller size of wear debris for the biodiesel-fuelled engine, suggesting inherent lubricity of the fuel. SPDSC tests suggested that oxidation stability of lubricating oils from the biodiesel-fuelled engine was slightly lower than that of diesel-fuelled engine.

All these tribological investigations, except SPDSC, decisively proved that the lubricating oil from the biodiesel-fuelled system reflected a better condition of the engine parts. Biodiesel thus proves to be a strong candidate for partial replacement of mineral diesel fuel in existing diesel engines.

ACKNOWLEDGEMENTS

The author is very grateful to Sh. Attar Singh of Engines and Fuels Laboratory, Centre for Energy Studies, IIT Delhi, for his help and association in conducting the torturous series of experiments. The help and assistance of Mr Deepak Agarwal, master's student of environmental engineering and management program of IIT Kanpur, in the preparation of this manuscript is also highly appreciated.

REFERENCES

1 **Agarwal, A. K.** Performance evaluation and tribological studies on a biodiesel fuelled compression ignition engine. PhD Thesis, Center for Energy Studies, IIT Delhi, 1999.
2 **Agarwal, A. K.** and **Das, L. M.** Biodiesel development and characterization for use as a fuel in compression ignition engine. *Trans. ASME, J. Engng Gas Turb. Power*, 2001, **123**, 440–447.
3 **Krawczyk, T.** Biodiesel: alternative fuel makes inroads but hurdles remain. *Inform*, 1996, **7**(8), 801–814.
4 **Devitt, M., Drysdale, D. W., MacGillivray, I., Norris, A. J., Thompson, R.** and **Twidell, J. W.** Biofuel for transport: an investigation into the viability of rape methyl ester (RME) as an alternative to diesel fuel. *Int. J. Ambient Energy*, 1993, **14**(4), 195–218.
5 **Freedman, B., Butterfield, R. O.,** and **Pryde, E. H.** Transesterification kinetics of soybean oil. *JAOCS*, 1986, **63**(10).

d000006204 24-02-05 09:34:20 Rev 14.05
The Charlesworth Group, Huddersfield 01484 517077

6 American Biofuel Association. Biodiesel: a technology, performance and regulatory overview. Information Resources, Washington D.C., 1994.

7 **Weber, J. A.** and **Johannes, K.** Biodiesel market opportunity and potential barriers. Edited by Wnditt, J. S., Gavett, E. E., Hansen, C., Peterson, C., Sanderson, M. A., Shapouri, H., and Van Dyne, D. A., Liquid fuels and industrial products from renewable resources, Proceedings of the third fuel conference, 15–17 September 1996, Nashville, TN, ASAE, 1996.

8 **Diasakou, M., Louloudi, A.,** and **Papayannakos, N.** Kinetics of the non-catalytic transesterification of soybean oil. *Fuel*, 1998, **77**(12), 1297–1302.

9 **Dotterer, G. O.** and **Hellmuth, W. W.** Differential infrared analysis of engine oil chemistry in sequence V tests, road tests, and other laboratory engine tests. *Lubric. Engng*, 1985, **41**(2), 89–97.

10 **Lee, H. S., Wang, S. S.,** and **Smolenski, D. J.** In-situ oil condition monitoring in passenger cars. *Lubric. Engng*, 1994, **50**(8), 605–611.

11 **Furey, M. J.** Film formation by an antiwear additive in an automotive engine. *ASLE Trans.*, 1959, **2**, 91–100.

12 **Feng, I. M.** Pyrolysis of zinc-dialkly-phosphoro-dithioate and boundary lubrication, *Wear*, **3**(1060), 309–311.

13 **Kawamaura, M.** The correlation of antiwear properties with the chemical reactivity of zinc-dialkyl-dithio-phosphates. *Wear*, 1982, **77**, 287–294.

14 **Smolenski, D. J., Shirley, E.,** and **Warren, S.** Automotive engine-oil condition monitoring. *Lubric. Engng*, 1994, 716–722.

15 **Ekanem, E. J., Lori, J. A.,** and **Thomas, S. A.** The determination of wear metals in used lubricating oils by atomic absorption spectroscopy using sulphanilic acid as ashing agent. *Talanta*, 1997, **44**, 2103–2108.

16 **Agarwal, A. K., Bijwe, J.,** and **Das, L. M.** Wear assessment in biodiesel fuelled compression ignition engine. *J. Engng Gas Turb. Power*, 2003, **125**(3), 820–826.

17 **Goncalves, I. M., Murillo, M.,** and **Gonzalez, A. M.** Determination of metals in used lubricating oils by AAS using emulsified samples. *Talanta*, 1998, **47**, 1033–1042.

18 **Bijwe, J., Garg, A.,** and **Gandhi, O. P.** Reassessment of change of engine oil periodicity in commercial vehicles. *Lubric. Engng*, 2000, **1**, 23–29.

19 **Lamotte, A.** and **Auvray, J.** Utilisation de la chromatographie sur couches minces pour l'analyse des additifs dans les huiles neuves et usagés. *J. Chromat.*, 1974, **97**, 213–222.

20 **Fitch, J. C.** Oil analysis and proactive maintenance. The Proactive Maintenance Institute, Diagnetics Inc. 1994.

21 **Bijwe, J., Agarwal, A. K.,** and **Sharma, A.** Assessment of lubricity of biodiesel blends in reciprocating wear mode. SAE paper 2002-01-2742 SAE powertrain and fluid systems conference and exhibition, October 2002, San Diego, CA, USA.

22 **Bowman, W. F.** and **Stachowiak, G. W.** Determining the oxidation stability of lubricating oil using sealed capsule differential scanning calorimetry (SCDSC). *Tribology Int.*, 1986, **29**(1), 27–34.

d000006204 24-02-05 09:34:20 Rev 14.05
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