

ICES 2003-609

Lubricating Oil Tribology of a Biodiesel-Fuelled Compression Ignition Engine

Avinash Kumar Agarwal

Assistant Professor

Department of Mechanical Engineering, Indian Institute of Technology, Kanpur

Kanpur-208 016 India

Email: akag@iitk.ac.in

Abstract

Biodiesel is an alternative fuel derived from vegetable oils by modifying their molecular structure through transesterification process. Linseed oil methyl ester (LOME) was prepared using methanol in the presence of potassium hydroxide as catalyst. Use of linseed oil methyl ester 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 optimum biodiesel blend (20% 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 comparative performance of the two fuels such as density measurement, viscosity measurements, flash point determination, moisture content determination, pentane and benzene insolubles, thin layer chromatography, differential scanning calorimetry etc. All these tests were used for indirect interpretation of comparative performance of these fuels. Biodiesel fuels performance is found to be superior to that of diesel oil and the lubricating oil life is found to have increased, while operating the engine on this fuel.

Introduction

Though the Kyoto Protocol has undoubtedly stressed on a cleaner environment, it is needless to reiterate the fact that sustainable development of our natural resources in this technologically galloping era goes hand-in-hand with the former. Sustainable development, synonymous with the directive 'proceed with caution', in a broader sense, implies the utilization of present resources in a proficient manner. Sustainable development includes, in its ambit, innovations ranging from recycled waste, biodegradable plastics, ozone-friendly technology, and fuel-efficient appliances to alternate fuels and renewable energy sources. 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. Ever since the advent of IC engines, vegetable oils have been tried as an alternative to diesel fuel. The inventor of the diesel engine, Rudolf Diesel, in 1885, used peanut oil as a diesel fuel for demonstration at the 1900 world exhibition in Paris. Speaking to the Engineering Society of St. Louis, Missouri, in 1912, Diesel said, "The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become in course of time as important as petroleum and the coal tar products of the present times". The same petroleum-based fuel used in Diesel's days is still the fuel of choice in modern motorised society [1]. The oil supply shocks in the 70's 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 for energy in the 70's, and again by the gulf war in 1991. The production-demand gap of fossil oils is declining worldwide and countries like India, being highly dependent on huge imports of fossil oil, are facing an increasing risk in the security of energy supply. Biodiesel development from renewable bio-origin crops was taken up for investigation in the present study.

Environmental Benefits

The recent research and development studies show that biodiesel demonstration programmes have focused on the markets that have the greatest chance of choosing biodiesel despite its higher cost. These markets place a premium on biodegradability, non-toxicity, lower emissions profile, and overall environmental benefits of biodiesel. Neat biodiesel is as biodegradable as sugar, and less toxic than salt. A research study at the University of Idaho shows that neat biodiesel degraded up to four times faster than petroleum diesel, and a blend (50% petroleum diesel and 50% biodiesel) biodegraded in one-third the time required by petroleum-based diesel fuel [2]. In addition, biodiesel offers lower exhaust emissions than diesel fuel. With a level of emissions 10%–20% lower CO, particulate matter, and unburned hydrocarbons, biodiesel is a "clean" fuel. Slight increased NO_x emissions (2%–4%), coupled with

decreased engine exhaust temperatures, have led researchers to believe that methyl esters, acting as fuel cetane improvers, result in a reduced ignition delay time, and thus an effective advance in injection timing. One method of dealing with biodiesel NO_x emissions is to retard the injection timing of the engine. However use of an oxidation catalyst, or catalytic converter, reduces emissions by oxidizing the soluble fraction of the fuel. Emissions can be reduced by more than 40% for total hydrocarbons, 30% for particulates, and 20% for CO. NO_x emissions can also be brought down to diesel baseline or below [3]. Another option that is being investigated is the use of fuel additives to control NO_x emissions. Additives to reduce NO_x emissions are being studied by NCAUR. The NO_x emissions of biodiesel are not so much of a problem, as it is only marginally higher than conventional diesel. A minor inconvenience should not detract from the numerous advantages that biodiesel offers [1,4].

Vegetable Oils

Vegetable oils have approximately 90% of the heat content of diesel fuel and they have a favourable output/input ratio of about 2 to 4: 1 for un-irrigated crop production. The current prices of vegetable oils in India are nearly competitive with petroleum fuel price. Some of these vegetable oils are readily available and are in fact, in surplus and under-utilised. The high viscosity of vegetable oils interferes with the injection process and leads to poor fuel atomisation. The accompanying inefficient mixing with air due to low volatility contributes to incomplete combustion. The high molecular weights of vegetable oils result in low volatility as compared to diesel fuel, which leads to the oil sticking to the injector or cylinder walls. Oil then undergoes oxidative and thermal polymerisation, causing a deposition on the injector, forming a film that continues to trap fuel and interfere with combustion leading to more deposit formation, carbonisation of injector tips, ring sticking, and lubricating oil dilution and degradation. The combination of high viscosity and low volatility of vegetable oils cause poor cold engine start-up, misfire, and ignition delay. Since viscosity is one of the key factors in making a fuel usable in diesel engines, the question then becomes not only of decreasing the viscosity, but also minimizing a lot of other undesirable properties from vegetable oils. This includes reducing the carbon chain length, increasing volatility and reducing the unsaturation of vegetable oil molecules [3]. The ideal diesel fuel molecule is saturated non-branched hydrocarbon molecule with carbon number ranging between 12 to 18, whereas vegetable oil molecules are triglycerides generally with straight chains of different lengths and different degrees of saturation. It may be seen that vegetable oils contain a substantial amount of oxygen in their molecular structure. Triglyceride molecules have molecular weights between 800 and 900 and are thus nearly four times larger than diesel fuel molecules. Because of their unsaturated character, i.e., presence of double bonds, vegetable oils are inherently more reactive than diesel fuels. Consequently, they are susceptible to oxidative and thermal polymerisation reactions, which cause deposits on the injector tip, forming a

film that continue to trap fuel and constantly interfere with combustion.

There are a number of serious reasons for using bio-fuels as alternative fuels, e.g., expected growth of prices of fossil liquid fuels in the near future, gradual exhaust of crude oil sources in the next 80–100 years, etc. Marginal land excluded from food production may be used for growing biodiesel crops [5].

Vegetable oil in its raw form cannot be used in engines. It has to be converted to a more engine-friendly fuel called biodiesel. Biodiesel is a chemically modified alternative fuel for diesel engines, derived from vegetable oil fatty acids, and animal fat. Biodiesel is a fuel made up of esters derived from oils and fats from renewable biological sources. It is well known that petroleum refiners are now facing new sulphur and aromatic compound specifications. It has been reported to emit far less regulated pollutants than petroleum diesel fuel along with lower sulphur and aromatic compound [6]. The carbon cycle time for fixation of CO₂ and its release after combustion of biodiesel is quite small (few years) as compared to the cycle time of petroleum oils (few million years).

Methanol and ethanol are two abundantly available alternative fuels, which possess the potential to be produced from biomass resources. These fuels, if combusted in engines directly emit harmful unregulated emissions containing formaldehyde and ketones, which create environmental nuisance. But these fuels can be successfully used as diesel engine fuels by preparing biodiesel. Transesterification process utilizes methanol or ethanol and vegetable oils as the process inputs. This route of utilizing alcohol as a diesel engine fuel is a definitely superior route as the regulated emissions as well as unregulated toxic emissions containing aldehydes are drastically reduced. The problem of corrosion of various engine parts, when utilizing alcohol as fuel, can also be tackled by way of transesterification [7].

Transesterification

Transesterification is probably the most effective and widely used technique for formulating the biodiesel for use in Compression Ignition (CI) engines. Transesterification was known as early as 1864, when Rochleder described glycerol preparation through ethanolysis of castor oil. Transesterification is a chemical reaction that aims at substituting the glycerol of the glycerides with three molecules of mono-alcohols such as methanol, thus leading to three molecules of methyl ester of the vegetable oil. The idea of chemically altering vegetable oils was noted even before World War II. Walton wrote in 1938 "to get the utmost value from vegetable oils as fuels it is academically necessary to split the glycerides and to run on the residual fatty acid" because "the glycerides are likely to cause an excess of carbon in comparison" [8].

Transesterification is a reversible reaction, which is either acid or alkali-catalysed, and involves stepwise conversions of triglycerides to diglycerides to monoglycerides to glycerol producing 3 molecules of ester in the process [9]. A mixture of anhydrous alcohol and reagent (NaOH) in desired proportions is combined with moisture-free vegetable oil. The

materials are maintained at 65–70°C and then allowed to settle by gravity for 24 hours for separation of esters and glycerol. These esterified oils can be produced in a chemical laboratory by the above method. The molar ratio of the reagents, the presence of water, and free fatty acid determine the effectiveness of catalyst. A higher molar ratio (6:1) favours the use of sodium hydroxide (NaOH) over sodium methoxide (NaOCH₃), while a lower molar ratio (3:1) favours the use of NaOCH₃. NaOH is cheaper than NaOCH₃ but must be present in excessive amounts. The vegetable oils must not contain traces of water and must have a low free fatty acid content. Alkaline catalysts have the advantage of being less corrosive to industrial equipment than acid catalysts. The transesterification process breaks the triglycerides in the vegetable oils into fatty acid esters and glycerol. 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 [3, 4, 10, 11, 12].

Engine Set-Up and Tests

Direct injection (DI) diesel engines are widely used in the agricultural sector; whether the machinery is mobile, as in tractors, transport vehicles or stationary such as in irrigation pump sets, farm machinery, etc. In consideration of some typical characteristics such as power developed, specific fuel consumption, and durability of diesel engines (as compared to spark ignition), they would still continue to dominate our agriculture sector.

Keeping the specific features of diesel engine in mind, a typical engine system, which is actually used widely in the Indian agricultural sector, has been selected for the present experimental investigations. These are two exactly similar compact, single-cylinder, and water-cooled, portable diesel engine gensets of 4 kW rating, each with an alternator. The engines were provided with suitable arrangement, which permit wide variation of controlling parameters. This engine is also widely used for many small and medium scale commercial applications.

Manufacturer	Perry Engines Ltd, India
Model	Single-cylinder CI engine
Bore	87.5 mm
Stroke	110 mm
Displacement	661.7 cm ³
Length	531 mm
Width	356 mm
Height	546 mm
Weight	165 Kg
Rated speed	1500 rpm
Maximum speed	2000 rpm
Minimum speed	1200 rpm
Minimum idling speed	750 rpm
Nozzle pressure	200 bar
Compression ratio	17: 1

Table 1: Technical specifications of the test engine

At the rated speed (1500 RPM), the engine develops 4 kW power output. The engine is flexibly coupled with a single-phase, 220 volts AC generator of sufficient capacity to absorb the maximum power produced. The inlet valve opens at 4.5° BTDC and closes at 35.5° ABDC. The exhaust valve opens at 35.5° BBDC and closes at 4.5° ATDC.

After developing biodiesel, it was tested on this engine for performance and emission characteristics. The concentration of ester in biodiesel blend was optimised using performance and emission considerations for several concentrations of biodiesel blends. 20% biodiesel blend was found to be optimum. The long-term endurance test specified by Indian Standards Code (IS: 10000, part VIII-1980, "Methods of tests for internal combustion engines: Part VIII Performance tests") was carried out with this optimised blend. In the long-term endurance test, the effect due to the fuel chemistry of biodiesel on various parts of the engine vis-à-vis mineral diesel oil was studied. For this purpose, two similar engines were subjected to similar loading cycles and operating conditions. The engines were dismantled, re-assembled, and mounted on a suitable test bed after dimensioning of various engine parts. The engines were run for 32 cycles (each of 16 hours continuous running) at rated speed. The test cycle followed is specified in Table 2.

Load (% of rated load)	Running time (hrs)
100	4 (incl. warm up for 0.5 hrs)
50	4
110	1
No load (idling)	0.5
100	3
50	3.5

Table 2: Test cycle for long-term endurance test

At the end of each 16-hour cycle, both engines were serviced and minor adjustments were made. The lubricating oil samples were collected from each engine after every 128 hours for conducting various tribological studies.

Lubricating Oil

Efforts are being made to increase useful life of lubricating oils as it alone costs approximately 6%–7% 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. The lubricating oil contains a solvent neutral base stock with a succinimide-type dispersant, a calcium-sulfonate-type detergent, olefin-copolymer-type viscosity index improvers, and a zinc-di-alkyl-dithio-phosphate (ZDDP) type antiwear and oxidation inhibitor [13]. The lubricating oil is consumed in the engine continuously, which needs to be replenished. The addition of fresh oil into the crankcase replenishes depleted additives and can temporarily improve oil condition. Hence, in addition to the length of service since the last oil change, the overall oil condition and oil degradation rate also depends on factors including engine condition, driving environment, oil consumption and oil addition rates [14].

A number of investigations have dealt with the mechanism of antiwear activity. Some researchers have proposed the formation of an extreme pressure (EP) film and others have proposed the formation of friction polymer. Furey [15] detected chemically bonded phosphorus on a valve lifter surface of an engine by using ZDDP labelled with ^{32}P . Feng *et al.* [16] proposed a polymer formation theory from the analytical results of thermally decomposed ZDDP. Since both mechanisms depend on thermally induced reactions, the reactivity of ZDDP with temperature rise may be an indicator for the antiwear property [17].

Tribological Studies on Lubricating Oil

Deterioration in the lubricating characteristics of oil is due to oil degradation and ageing because of prolonged, repeated mechanical, thermal, environmental stresses and contamination with foreign particles. Interestingly all these factors are inter-related and work synergistically to worsen the oil condition. Oil degradation, which refers to irreversible changes, happen to the oil itself. The reasons for oil degradation may be any of the following.

- Oils are prone to oxidation: In spite of various multifunctional additives, oil undergoes slow oxidation. Oxidation products get polymerised into resins, aldehydes, and ketones, etc., and finally into corrosive acids.
- Depletion of additives: There are various types of additives, e.g., some are multifunctional such as ZDDP. These are basically sacrificial in nature and protect oil by retarding the rate of oxidation substantially. The moment they are depleted, oil oxidation becomes uncontrollable.
- Contamination: It can be because of external and internal particles as well. Some common contaminants are fuel combustion products, e.g. soot particles, solid particles like dust, sand particles, and metallic wear debris from the various moving parts and liquid contaminants like water, other grades of lubricating oil, and fuel.

Analysis of used lubricating oil is a very effective tool for condition monitoring of an engine. Apart from this, oil analysis is a very powerful technique for failure analysis, diagnostics and preventive maintenance. In the present investigation, oil analysis has been employed as a tool to examine engine performance for different fuels. Oil samples were drawn from the running engines (both the systems, i.e., fuelled by diesel and biodiesel under similar operating conditions) after fixed interval of time (every 128 hours). It was anticipated that biodiesel, being, a derivative of vegetable oil which has inherent lubricity properties, will affect the engine performance, and this will be reflected in the lubricating oil analysis.

Prior to adopting any alternative fuel for regular use in the conventional engines, it is essential that the tribological studies related to lubricating oil with biodiesel fuel must be studied. A review of literature shows that such studies have hardly been carried out. An extensive analysis has been carried out in the present work to technically justify the regular use of biodiesel for engine application. Various tribological studies

have been conducted to assess the comparative effect of fuels on the engine's health.

A number of factors affect engine oil performance. Oil thickening, loss of wear protection additives, and deposit controls are of concern primarily in high temperature, and high loading conditions. Oil thinning, loss of corrosion protection, and low temperature sludge formation are of concern primarily in short engine runs, which may also cause particular type of engine oil degradation [18]. Analysis of used engine oil could yield worthwhile information such as the condition of the oil, the engine condition and early detection of problems in the absence of an inspection, and probable causes of problems or failure observed when actual engine inspections are performed.

Several other analyses often used to characterize engine oils, primarily in quality control checks or special applications include specific gravity, density, brookfield specific gravity, density, brookfield viscosity, pour point, flash point, distillation characteristics, sulphated ash, chlorine, sulphur, nitrogen, oil insolubles, TAN/TBN, moisture content, chromatography, calorimetry, and Ferrographic analysis etc [18]. To date, several other bench tests are available to evaluate deposits, including penn-state micro-oxidation test, ASTM coking method, hot-tube test, ashing test, texaco hot panel test, panel coker test, and mobil spinning disc test etc. While most of these methods have been adopted in one form or another by industry, the accuracy, repeatability, and correlation of the results of engine test results are often limited due to the shortcomings of the methods. In addition, some of them are manpower intensive [19].

The following tests were selected in the present investigations to assess the condition of the engine oil drawn from diesel and biodiesel fuelled engines. Density, kinematic viscosity, ash content, water content, flash point, pentane and benzene insolubles, IR spectroscopy, SPDSC/SCDSC, TLC, AAS, and DR ferrography for wear debris analysis. These exhaustive tests provide valuable information on the effect of fuel chemistry of biodiesel on the lubricating oil vis-à-vis diesel oil.

Viscosity test is a very basic test and is highly recommended for routine inspections. It confirms that the correct product for the equipment is in place, with respect to viscosity. A corollary of this is the assurance that incorrect viscosity product is not being added, and can confirm severe cases of oxidation (thickening).

Fuel contamination in engine oil (fuel dilution) can be determined by either of ASTM methods D322 or D3525. Since method D322 can erroneously indicate fuel contamination in fresh oil samples, D3525 is generally preferred. Excessive unburned fuel in the oil can reduce oil viscosity and reduce oil-film thickness thus increasing chances of metal-to-metal contact at piston ring-liner interface of the engine. Fuel in the engine oil reduces oil viscosity and may lead to insufficient fluid films in bearings. If ambient temperatures are moderate to high and trips are sufficiently long, then the oil reaches equilibrium operating temperatures. Substantial amounts of fuel in the oil (greater than about 3%) indicate a possible malfunction in the vehicle fuel supply system [18]. If there is an engine malfunction that allows antifreeze (ethylene glycol, water, and additives) to

leak into the oil, testing for glycol becomes important. The presence of glycol can be detected by several methods such as ASTM D 2982 or D 4291. Glycol contamination in engine oils can cause sludging and more rapid ageing of the oil. Some oil additives and oil contaminants such as aldehydes can produce a positive test for glycol when, in fact, no glycol is present [18].

Thin layer chromatography (TLC) was carried out to evaluate the residual concentration of ZDDP in the used oils. The oil samples are diluted to one percent using hexane solution and this solution was spotted on a Merck pre-coated silica gel plate. The plate was first developed with hexane, and then with mixed solvent consisting of hexane: acetone: di-ethylamine: ammonia water in the ratio 200: 100:: 205: 2. Palladium chloride diluted with 5N hydrochloric acid was sprayed as a colour-producing reagent. The intensities of the spots were evaluated by means of thin layer densitometer. On the basis of the spot intensities of ZDDP in the fresh oils, the residual concentrations in the used oils were evaluated [17]. Lamotte et al. proposed several absorbent-solvent combinations for the chromatography of organo-phosphorous compounds in motor oils. Precise experimental conditions are specified, which are necessary in order to obtain good results. It is possible to identify di-thio-phosphates and the degradation products, mono-thio-phosphate and phosphate, in these used oils [20].

The determination of these metals in lubricating oils has always been a challenge in analytical chemistry. Metals such as Ba, Ca, and Mg, etc. are added to the lubricating oil, as organo-metallic compounds, to improve the colour, pour point, viscosity, antiwear, antifrictional, antifoaming, oxidation, corrosion inhibition properties and oil performance under severe conditions [21]. In addition, metals such as Fe, Al, Cu, Zn, Co, and Ni get suspended in used oil due to friction and wear of the lubricated area. Therefore, determination of the metal content in used oils is important to identify and repair any possible defective functioning area of the oil lubricated equipment and to schedule maintenance accordingly. Specific application of analysis of used lubricating oils is to indicate potential failure in IC engines. These used oils have potential for metal pollution, if they are disposed directly into surface water or on land. Although wear metal particles are not uniformly distributed in oils, they are generally determined by using techniques traditionally applicable to the determination of metals in homogeneous solutions. Modern instrumental techniques such as inductively coupled plasma-optical (ICP) emission spectrometry and atomic absorption spectroscopy (AAS) have been widely used for this analysis [22].

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. The differential scanning calorimetry (DSC) technique determines the concentration of degradation products in the oil such as oxidation and nitro-oxidation products, additive depletion, and contamination [13]. Electrical conductivity measurements were conducted on various passenger car motor oils and natural gas fuelled engine oil for the purpose of developing a real time sensor for the life of oils. The conductivity is found to be affected by the characteristics of aggregated micelles formed by detergent additives. A good correlation between behaviour of

conductivity and the neutralization values of oils has been established by Atsushi *et al.* [23]. In addition, some micro-sensor testers have been developed for *in situ* monitoring of the oil. DSC calorimetry and cyclic voltametry for evaluating residual useful life (RUL) of the oil have also been used. SPDSC (sealed pan differential scanning calorimetry) technique however is the most recent, and has been applied for evaluation of RUL of oil under induced thermo-oxidative stresses in the laboratory. Bijwe et al. applied this technique, in conjunction with some other commonly used techniques for condition monitoring of the engine oil of two commercial vehicles and also to identify safe and unsafe zones for oil operation [24].

The oxidation and combustion of lubricating oils often result in the formation of insoluble deposits on the metal surfaces in combustion engines. Accumulation of sludge and varnish deposits on engine parts cause poor lubrication and increased engine wear, therefore, the deposit-forming tendency of oils is one of the major concerns in oil evaluation [20]. However, some insolubles are deliberately introduced by the manufacturer to improve the performance of the lubricants [25].

Results of oil Tribology Investigations

The lubricating oil samples were drawn after every 128 hours from the two engine systems operating on diesel and 20% biodiesel blend fuels, respectively. The samples were drawn according to standard sampling procedure.

It has already been discussed that adequate experimental data is still not available on the tribological investigations of using biodiesel in a CI engine. No single test is self-sufficient and various tests are to be exploited to get a complete picture of the health of lube oil. Experimental results of several tests conducted have been discussed in the following paragraphs.

Density

Density measurements are important since they provide information on the addition of wear metals and fuel dilution in lubricating oils. The density of lubricating oil samples from biodiesel- and diesel-operated engines were measured, and a graph was plotted for density vs. hours of lube oil usage.

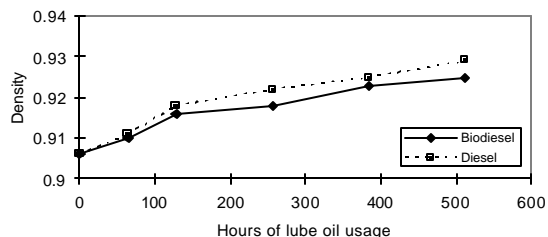


Figure 1: Density vs. hours of lube oil usage

The density of lubricating oils from both the engines show an increasing trend with the usage. The density increased

faster in the initial phase of engine operation. The rate of increase in density decreased after 128 hours of engine operation. It can be noticed from figure 1 that the density of lube oils from diesel-operated engine increased at a faster rate, which may be due to the following reasons.

- The wear debris addition in lube oil from biodiesel-operated engine may be lower.
- The fuel dilution in the case of biodiesel-operated engine may be lesser as biodiesel may be helping reduce the blow-by losses of fuel to oil.
- The addition of moisture to lube oil from the blow-by gases may be lower in case of biodiesel-operated engine for the same reason.

These reasons indicate that the addition of biodiesel to mineral diesel oil improved the density change pattern in the lubricating oil. However, the most important observation of this study was that biodiesel-fuelled engine oil had lesser deterioration in density throughout the entire range of engine operation thereby indicating lower wear of vital engine components.

Ash Content

Ash content reflects non-carbonaceous material in the lubricating oil (Carbonaceous materials such as oil, soot, fuel and non-metallic parts of additives convert into CO₂ after thermal decomposition). Ash content mainly indicates metallic wear debris and abrasive foreign particles like sand entering the system. Since both of the systems were operated under identical conditions, the contribution of foreign particles may be safely assumed to be similar. Any variation in ash content in the present investigation primarily reflects the effect of fuel chemistry and its effect on the amount of wear debris in the lubricating oil.

The data on ash content in the lubricating oils for biodiesel and diesel fuelled compression ignition engines is presented in figure 2. It was observed that the ash content for biodiesel-operated engine oil was approximately 15% lower than that of diesel-operated engine oil. Any variation in the ash content in the present investigation mainly indicate the extent of wear debris and subsequently engine performance. It is evident that biodiesel fuelled engine produced lower amount of metallic wear debris.

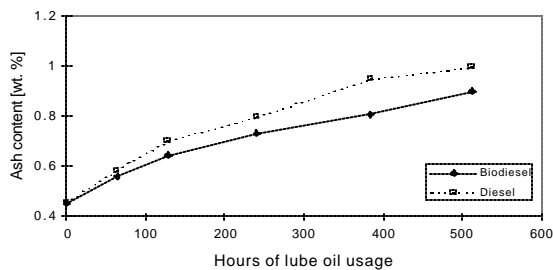


Figure 2: Ash content vs. hours of lube oil usage

Viscosity

Any change in viscosity is undesirable in the system as it affects the lubricating efficiency of the oil. In fact, the criterion for the change of lube oil states "change the lubricating oil if viscosity increases by 20% or more, or decreases by 10% or more"[26]. With the usage of lubricating oil, the viscosity may increase or decrease. Inadequate oil viscosity affects film formation and load bearing capacity leading to excessive wear of bearings, journals, other moving components, low oil pressure, and poor oil economy. There are two main factors responsible for the viscosity changes affecting the oil in opposite directions.

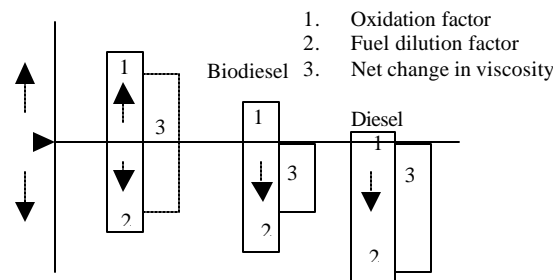


Figure 3 Mechanism responsible for net change in viscosity of oil

Formation of resinous products because of oil oxidation, evaporation of lighter fractions, depletion of antiwear additives, and contamination by insolubles tend to increase the viscosity while fuel dilution and shearing of viscosity index improvers tends to bring down its viscosity. The extent of dominance of both the mechanisms, however differ from system to system. Hence, the net result can be reflected in either direction as shown in figure 3. If the first factor is dominating and the possibility of fuel dilution is negligible, then the viscosity value increases. Sometimes viscosity can decrease, if fuel dilution is a dominating mechanism. The viscosity of all lube oil samples were evaluated at 40°C and 100°C using Setavis kinematic viscometer. The experimental results at these temperatures are shown in figures 4 and 5 respectively.

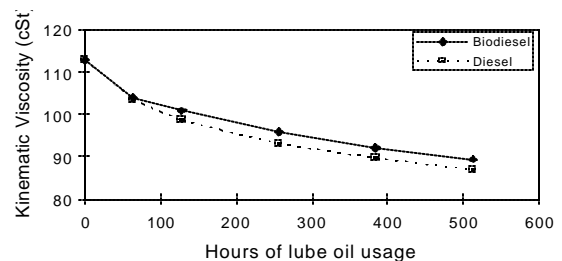


Figure 4: Kinematic viscosity at 40°C vs. hours of lube oil usage

An important observation was that the extent of lowering of viscosity of the lube oil is lesser in the case of biodiesel-fuelled system compared to diesel-fuelled system. This may be because of lower fuel dilution. Fuel dilution is a direct consequence of clearance between piston rings and cylinder liner. The more piston rings wear, more will be the clearance, and hence higher fuel dilution. Since biodiesel has inherent lubrication properties, it helps in protecting the piston rings from wearing out more effectively [27]. The viscosity of biodiesel helps in plugging the clearance between piston rings and cylinder liner effectively, thus reducing blow-by losses and fuel dilution of lubricating oil. Biodiesel has thus proved to be more effective in protecting the moving parts of the engine.

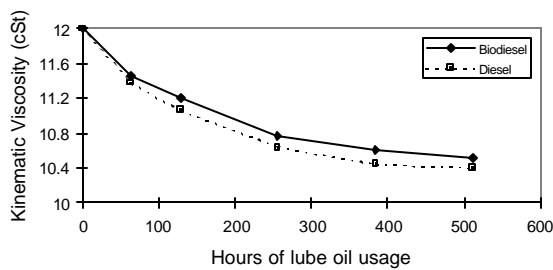


Figure 5 Kinematic viscosity at 100°C vs. hours of lube oil usage

The subtle point in this viscosity behaviour, however, cannot be neglected. As already discussed, the rate of change of viscosity is also controlled by another mechanism, viz., oil oxidation. In this case, it is also possible that the biodiesel fuel once entered in the lube oil could have accelerated the rate of oxidation of base stock leading to slightly higher viscosity. Hence, the decrease in viscosity due to fuel dilution could have been hampered. This fact was supported by FTIR studies, showing higher oxidation of base-stock in case of biodiesel-fuelled engine oil as explained in subsequent research work [3].

Flash point

The flash point temperature of all the lubricating oil samples was evaluated using the Pensky-Martens apparatus. For converting oil into the vapour phase, energy has to be supplied as heat. The oil fuel molecules experience van der Waal's forces on each other. Higher the extent of van der Waal's forces, higher will be the energy required for vaporizing and higher will be the flash point. Fuel dilution in the lube oil is undesirable because water and acids (which are responsible for oil degradation) often accompany fuel. Indeed, this was observed in the present study too. If lubricating oil is diluted with fuel in different proportions, the net effect on van der Waal's forces will also be different. If the dilutant is more, it will reduce the van der Waal's forces to a higher extent, and hence the oil can be evaporated easily.

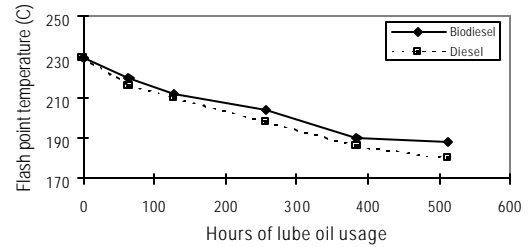


Figure 6: Flash point vs. hours of lube oil usage

As observed in figure 6, the flash point of oils from both the systems decreased with its usage. The extent of decrease, however, was approximately 5% lower for biodiesel-fuelled system. As observed previously also, fuel dilution was also found to be higher for diesel-fuelled system. The flash point of mineral diesel oil (76°C) is lower than biodiesel blend (128°C). Hence, dilution of lube oil with fuel of lower flash point should reduce the flash point of the lubricating oil to a higher extent. In the present investigation, since fuel dilution is more in case of diesel-fuelled system, hence the oil from this system shows lower flash point.

Moisture content

Moisture content was determined using ASTM D 1744 procedure. Water in the lube oil samples was determined by Karl Fischer titration method. Traces of moisture are intolerable as water contamination in engine oil can cause increased corrosiveness inside engine. Water also causes "additive drop out", i.e., precipitation of additives from the oil. Water in the lube oil may also indicate excessive fuel dilution, glycol leakage, and short trip driving. Mettler DL18 Karl Fischer titrator was used for determination of moisture content in the present investigation. The experimental results are shown in figure 7.

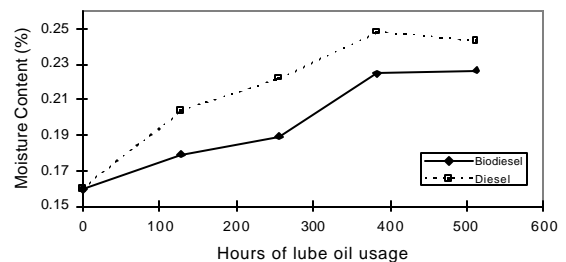


Figure 7: Moisture content vs. hours of lube oil usage

Approximately 15% lower moisture content is observed in the lubricating oil from biodiesel-fuelled system. It can also be seen that the initial rate of absorption of moisture was quite high, which stabilized after 400 hours. Lower amount

of absorption of moisture by the lubricant from biodiesel-fuelled system may also be an indirect consequence of additional lubricating property exhibited by biodiesel.

Pentane and Benzene Insolubles

The technique for calculating insolubles reflects the amount of sludge formed in the used oils. Used oils generally contain the following suspended contaminations of various sizes.

1. Oil soluble resinous material as a result of degradation of oil, additives or both
2. Fuel carbon or highly carbonized materials
3. Corrosion and wear particles from engine
4. Particles entering from the environment

The analyte, however, does not contain deposits/ layers formed in the system or large size contaminants since they are already removed during sample preparation.

Mainly two types of methods are used for insoluble determination. If the used oil contains detergents, then coagulants are used while determining insoluble. The coagulant agglomerates fine suspended particles also. Insoluble can be calculated without using coagulants and if the values are less then it indicates readily separable matter. (In the present investigation, coagulants are not used). The method is further divided as pentane insolubles and benzene insolubles. Both the solvents have different chemical structure hence preferential solubility for various materials is present. Pentane is aliphatic in nature and dissolves only lubricating oils. The resinous materials, which were otherwise soluble in oil, were thrown away as insolubles. The insolubles in this case contain all the ingredients as in (1), (2), (3), and (4). Benzene is aromatic in nature. It also dissolves resinous material along with oil, hence the separated insolubles contain ingredients as described in (2), (3) and (4). The weight of insoluble in benzene is lower than that of pentane. The difference between in pentane insolubles and benzene insolubles indicate the extent of oil oxidation. Higher the difference, higher is the oil oxidation, and lower residual useful life.

The method followed in the present investigation for determining insolubles is described in ASTM D 893-63. Apparatus required for the test are centrifuge, centrifuge tubes with corks, solvents, and balance. This test was conducted using Remi oil centrifuge. Three oil samples were tested for benzene and pentane insolubles at a time. Approximately 10 grams of accurately weighed oil were put in each of the six tubes. These oils were topped up to 100 ml mark with pentane/benzene. Centrifuge was operated at 1500 rpm for 20 minutes. The insolubles get deposited at the bottom of the tubes. Supernatant fluid was thrown away taking proper care not to disturb the cake formed in the bottom. This procedure was repeated with pentane/ benzene and the machine was run for 20 minutes at 1500 rpm again. Lastly, ethanol was added up to

10 ml mark and samples were subjected to centrifugation for 10 minutes at 1500 rpm. The tubes were finally dried in the oven at 150°C for 3 to 4 hours, and then weighed. The difference of weight measures the amount of insolubles present in the oil sample.

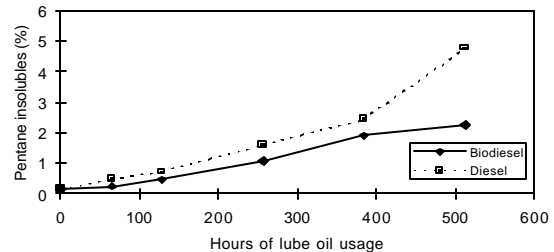


Figure 8: Pentane insolubles vs. hours of lube oil usage

Pentane insoluble indicate approximate amount of sludge formed by oil oxidation, metallic wear debris, soot particles as a consequence of fuel carbonization, and foreign particles entering the system. Higher insolubles also indicate inadequate efficiency of dispersants. Small passages may get blocked leading to deposition of sludge. Pentane insolubles as a function of lube oil usage are shown in figure 8. It can be noticed that biodiesel-fuelled system indicated lower amount of insoluble (Approximately 40% lower up to 400 hours and 60% lower after 400 hours of lube oil usage). Superior performance of biodiesel-fuelled system is reflected in terms of better condition of lubricating oil. Sudden shooting up of pentane insolubles beyond 400 hours in the case of diesel-fuelled system may be because of excessive oxidation of the base stock. The biodiesel fuelled engine oil is more prone to oxidation. Higher amount of difference in pentane insolubles in oil from diesel and biodiesel fuelled systems can be correlated as follows: first, diesel fuel does not have inherent lubricating properties as in case of biodiesel and second, excessive depletion of antiwear and extreme pressure additives. It has also been reported [18] that excessive moisture in the system is responsible for washing away such additives. This is actually observed in the moisture content experiments that the diesel-fuelled system absorbs higher moisture.

Benzene insolubles mainly indicate all of pentane insoluble except resinous oxidation products of lubricating oil. In fact, it's a better indicator of wear debris produced during engine operations if other contaminants such as sand particles, and carbonaceous matter are not changing. Results on benzene insolubles of lubricating oils of both the systems are shown in figure 9. The difference in the benzene insolubles becomes significant beyond 300 hours of oil usage.

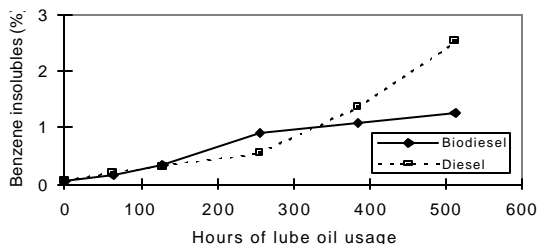


Figure 9: Benzene insoluble vs. hours of lube oil usage

In biodiesel system, benzene insolubles increased with a slow and steady pace, while in the case of diesel-fuelled system, it increased excessively beyond 300 hours. The obvious reason for this behaviour is excessive increase in wear of vital components of diesel engine. Low wear of vital components of biodiesel-fuelled engine again points towards inherent lubricity properties of the biodiesel. These findings are supported by the actual measurements of vital moving engine components for wear and also by ash content measurements [28].

Thin Layer Chromatography

TLC can rapidly provide information on the additives in a drop of oil, which may be time consuming or very difficult to get by any other technique. The infrared spectrum of oil containing several additives may be very complex to interpret and sometimes because of very low concentrations, very small peaks appear making analysis very difficult. Whereas TLC of the same oil rapidly separate the additive components and with the help of specific indicating reagent, information on the type and approximate quantity can be ascertained.

Thin layer chromatography is an effective technique for estimating the depletion of additives. In this study TLC has been used for estimation of depletion of ZDDP with the usage of lubricating oil and its comparative analysis for diesel- and biodiesel-fuelled system. Zinc di-alkyl-di-thio-phosphate (ZDDP) is well known as a multifunctional additive for motor oils. It combines antiwear, anti-oxidation, detergent, and corrosion-inhibiting properties.

The procedure is explained in the following steps.

1. Activated silica-gel-coated TLC plates were used for analysis.
2. Tests were conducted with different types of revealing reagents, i.e., palladium chloride and rhodamine B. Different mobile phase systems are required for each type of revealing agent as mentioned below.

Palladium chloride: Acetic acid + ethyl acetate + iso-octane (15 + 25 + 60) vol.%

Rhodamine B: Toluene + methyl ethyl ketone + acetic acid + pyridine (60 + 20 + 10 + 10) vol.%

3. Preparation of two indicating reagents is given below.

Palladium chloride: 1.5 grams of palladium chloride powder was dissolved in a mixture of water + acetone (50 ml + 50 ml).

Two drops of concentrated HCL was added, and the solution was kept for 24 hours before use.

Rhodamine B: 50 mg of Rhodamine B powder was dissolved in 100 ml ethanol. It could be immediately used.

Drops of approximately 2–5 micro litres of oil were placed on the activated silica-gel-coated TLC plates, at approximately 1 cm away from the lower edge. The plate was then placed vertical in the mobile phase in TLC jar in such a way that just 0.5 cm height was dipped in mobile phase. Care was taken not to dip the portion of oil drops in mobile phase and plate was taken out when mobile phase reached approximately 80% height of the plate. It was then air dried for 30 minutes. Indicating reagents were sprayed to give indication of ZDDP. In the case of palladium chloride, the presence of ZDDP was indicated through appearance of yellow brown spots on plate buff background. In case of rhodamine B, the presence of ZDDP was indicated by appearance of mauve spots on a pink background.

In addition, calibration was also attempted with known concentration of ZDDP using palladium chloride as the indicating reagent. For the calibration, various concentrations (0.1%, 0.2%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5%, and 3.0%) of ZDDP were mixed with oil base stock and chromatographs were developed by the procedure described earlier.

The corresponding chromatograms are shown in figures 10 and 11, respectively.

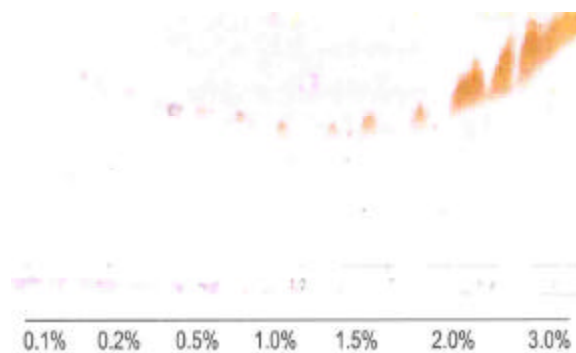


Figure 10: TLC of lubricating oils having various concentrations of ZDDP using PdCl₂ as revealing agent

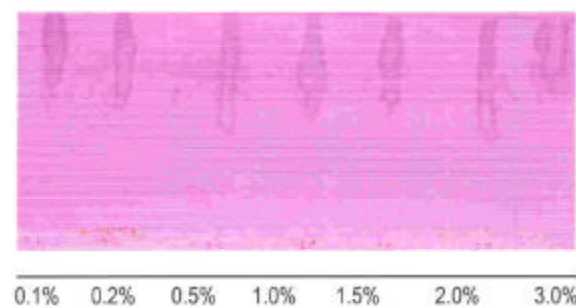


Figure 11: TLC of lubricating oils having various concentrations of ZDDP using Rhodamine-B as revealing agent

It can be clearly seen from the chromatogram based on PdCl_2 , that the intensity of brown coloured spots increased sequentially with the increase in ZDDP concentration. Similarly, the second chromatogram based on Rhodamine B also showed increasing intensity of mauve coloured spots with increase in concentration of ZDDP. The results of both the experiments confirm that the intensity of spots can reliably be correlated with the amount of ZDDP additive in the lubricating oil.

The PdCl_2 chromatograms developed for used engine oils are shown in figures 12 and 13 for diesel-fuelled engine and biodiesel-fuelled engine, respectively. The chromatograms clearly indicated that on increasing usage, the intensity of brown spots on puff coloured background kept on decreasing indicating more and more depletion of additives. It is also noticed that the additive did not get completely depleted in case of lube oil from biodiesel-operated engine. On the contrary, oil from diesel-fuelled system did not show appreciable amount of ZDDP beyond 378 hours of engine operation. Even in case of rhodamine B system (figures 14 and 15), similar results were observed, while confirming faster rate of depletion of additives in case of lube oils from diesel-operated engine. These results support the findings of the earlier studies, that the extent of wear is significantly low in case of biodiesel-fuelled system. This study suggest that for diesel-fuelled engine, the wear rates are higher because additive package depletes at a faster rate. Lubricating efficiency of biodiesel fuel and fuel chemistry has played an important role in depletion of lubricating oil additives, which control the performance properties of oil.

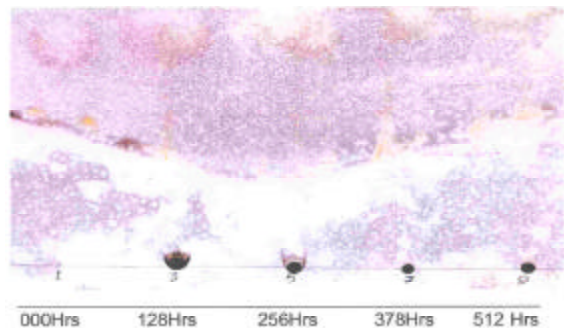


Figure 12: TLC of lubricating oils from Diesel engine using PdCl_2 revealing agent

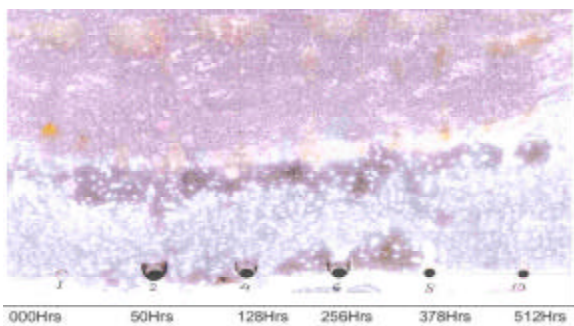


Figure 13: TLC of lubricating oils from Biodiesel operated engine using PdCl_2 revealing agent



Figure 14: TLC of lubricating oils from diesel operated engine using Rhodamine-B revealing agent



Figure 15: TLC of Lubricating Oils from Biodiesel operated engine using Rhodamine-B revealing agent

Analytical Ferrography

Wear is defined as the progressive loss of substance from the operating surface of a body occurring as a result of relative motion of the surfaces. It's a slow but continuous process of removal of material from one or more elements. Wear depends on load, speed, temperature, hardness, surface finish, presence of foreign materials, and environmental conditions. Wear particle analysis is a powerful technique for non-intrusive examination of the oil-wetted parts of a machine. The wear particles present in the lubricating oil carry detailed and important information about the condition of the machine.

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 form of wear and wear mechanisms. Wear particle analyses of the lube oil can therefore be used as a tool for monitoring not only the health of engine oil but moving parts also. This was a two-step process. The first step is slide preparation and second step is particle analysis. Bichrome microscope was used for particle analyses. Origin of the particle could be inferred from the composition of the particles e.g. indications of bronze, copper or a special type of steel may be traced to specific bearings.

DR ferrograph by Fox Boro/ Trans-Sonics Inc. was used for the present analysis. The basic element in the system is the ferrogram, which is prepared by pumping an oil sample across a slide or a substrate. The slide is mounted at an angle above a magnet so that the field varies along the length of the slide. Any substance within the oil sample that can be

magnetically attracted is held on the substrate. Field variations cause the particles to distribute themselves by size along a narrow band about 50 mm long. After the sample cascaded across the slide, the slide is washed with a fixative chemical that locks the particles in place and float away all other materials. Ferrograms reportedly picks up particles ranging in size from 20 nm to several hundred microns.

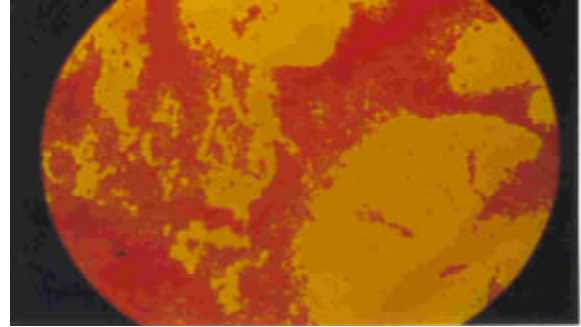


Figure 19: Ferrogram showing wear debris in lube oil from biodiesel engine after 256 hours of usage

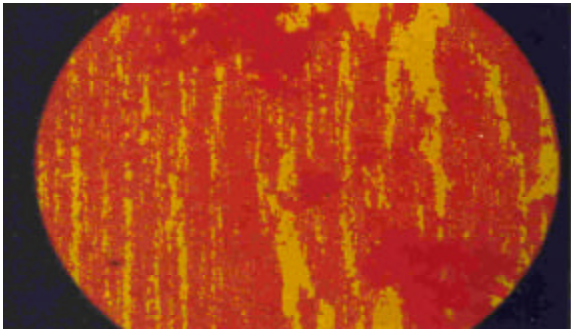


Figure 16: Ferrogram showing wear debris in lube oil from diesel engine after 128 hours of usage

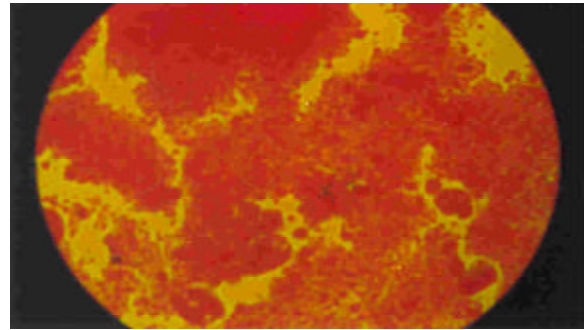


Figure 20: Ferrogram showing wear debris in lube oil from diesel engine after 386 hours of usage

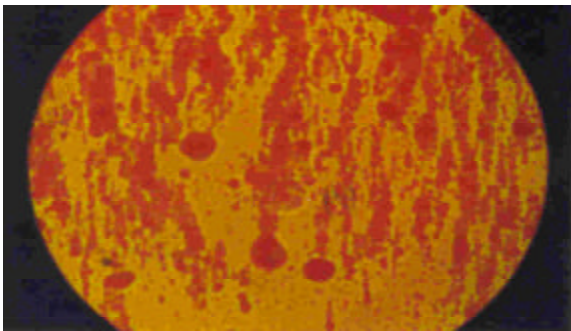


Figure 17: Ferrogram showing wear debris in lube oil from biodiesel engine after 128 hours of usage

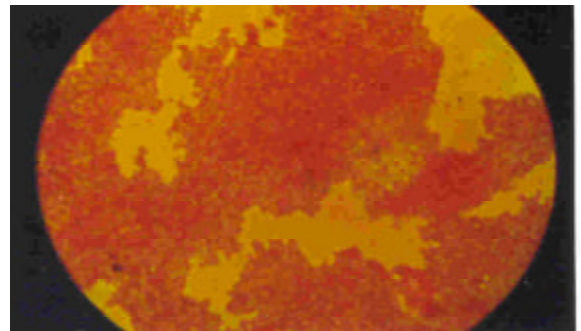


Figure 21: Ferrogram showing wear debris in lube oil from biodiesel engine after 386 hours of usage

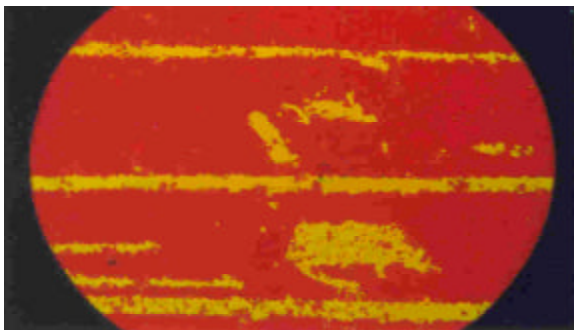


Figure 18: Ferrogram showing wear debris in lube oil from diesel engine after 256 hours of usage

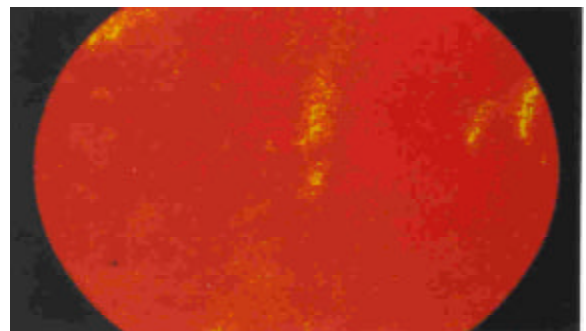


Figure 22: Ferrogram showing wear debris in lube oil from diesel engine after 512 hours of usage

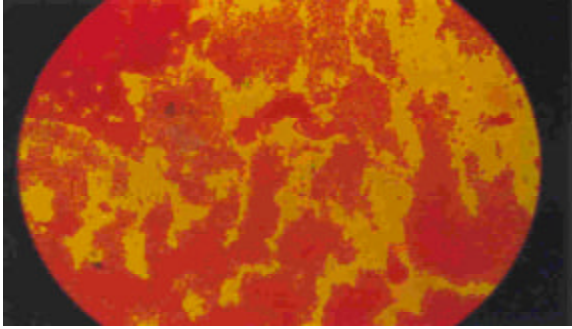


Figure 23: Ferrogram showing wear debris in lube oil from biodiesel engine after 512 hours of usage

For detailed analysis, a bichromatic microscope was used. With this instrument, light through a red filter is reflected from the top of the ferrogram and green filtered light was projected from the bottom. Transparent to translucent particles appeared green to red. Red light transmitted from above the slide and reflects backward (metallurgical lighting), shiny and reflective particles (e.g., free metal) appeared red. White and polarized light further helps in identifying particle species and origin.

Initial studies on ferrography have been collected in the form of ferrograms as shown in figures 16 to 23. It was clear from photographs that ferrous particle density increased with the increase in oil usage level. Overall visual inspection of ferrograms clearly indicate the difference in amount and type of wear debris in the biodiesel- and diesel-fuelled system. In the case of biodiesel-fuelled system, the size of wear debris is significantly smaller compared to diesel-fuelled system. This is a reflection of superior lubricating properties of biodiesel, which prevents wearing out of components to some extent. In the case of diesel-fuelled systems, which doesn't have such special lubrication properties, wear debris of larger size are observed. Bigger wear debris act like abrasive particles and damage the system further resulting in more and more wear of components with higher usage of oil. From earlier discussion, It is observed that beyond 400 hours, the wear increased excessively in case of diesel-fuelled engine.

Sealed Pan Differential Scanning Calorimetry

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. Recently, the use of differential thermal analysis (DTA) and more extensively, differential scanning calorimetry (DSC) has been applied to measure the stability of range of lubricants and antioxidant packages. Good correlation has been observed for characterising the deposit forming tendencies of diesel oils with their engine performance. DSC has also been used to propose a kinetics model for tri-acetyl-phosphate 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 existing DSC chamber to incorporate high pressures, use of a separate pressurised cell, and use of oxygen purged sealed pan or capsule. The SPDSC is the least developed method yet, which has the advantages of a lower instrumental cost and an easier operational technique in comparison to its high-pressure counterparts [29].

Here, SPDSC is used to measure the oxidation induction time (T_i) and oxidation stability of engine oil. Generally the shorter the induction time, lower is the thermal stability of the oil. DSC induction times are reduced by the presence of fuel in the oil and are influenced by the temperature at which the DSC test is conducted. The capsule pan, screw on lid, and gold-plated copper seal were cleaned thoroughly in acetone, and then dried. The tests were conducted on Du-Pont equipment. Aluminium pans were filled with 20 micro litres of used oil samples to be tested and were sealed while pouring oxygen. Test parameters selected were as follows.

Start Temperature = 140°C

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

Sealed pan was placed with the reference capsule (which remained unopened for all tests) in the DSC cell. The cell was closed and the system equilibrated at 50°C. The temperature of the cell was then ramped at 10°C/min (this represents the capsule's maximum recommended heating rate) until the designated start temperature (140°C) was reached. The temperature was then increased at a reduced ramp rate until a thermogram representative of the onset oxidation or induction time [29].

The prepared thermograms were compared for their oxidative stability. The thermograms for the two systems, i.e., diesel- and biodiesel-fuelled systems were compared with the thermograms for the fresh oil separately. Various thermograms of the lubricating oils drawn from diesel and biodiesel-operated systems are collected in figure 24 to figure 30. A graph is drawn between initiation temperatures of oxidation peaks in these thermograms vs. hours of lube oil usage as shown in figure 31. This curve reveals information about the destabilisation route of the lubricating oils with usage for both the engine systems.

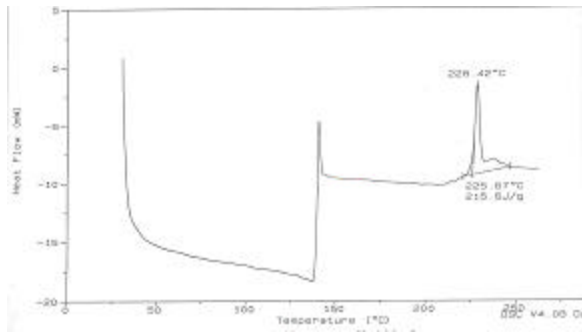


Figure 24: SPDSC thermogram of fresh lube oil

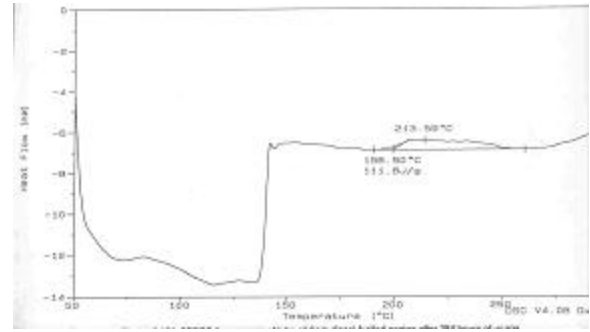


Figure 28: SPDSC thermogram of lube oil from biodiesel-fuelled engine after 256 hours of usage

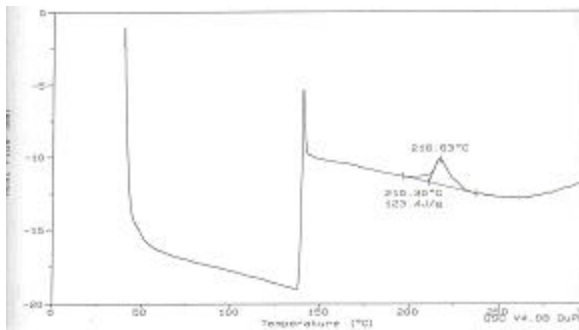


Figure 25: SPDSC thermogram of lube oil from diesel-fuelled engine after 128 hours of usage

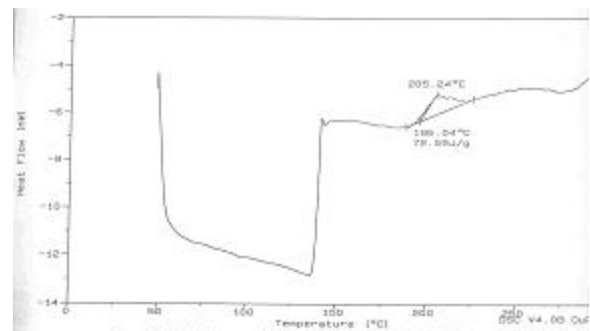


Figure 29: SPDSC thermogram of lube oil from diesel-fuelled engine after 384 hours of usage

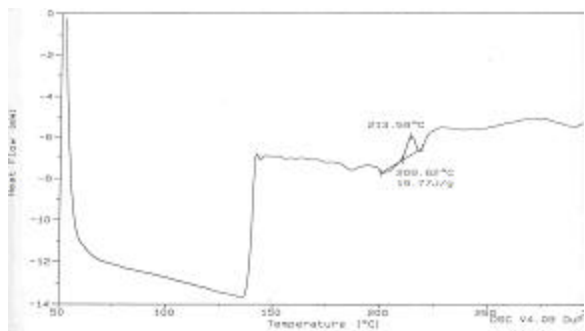


Figure 26: SPDSC thermogram of lube oil from biodiesel-fuelled engine after 128 hours of usage

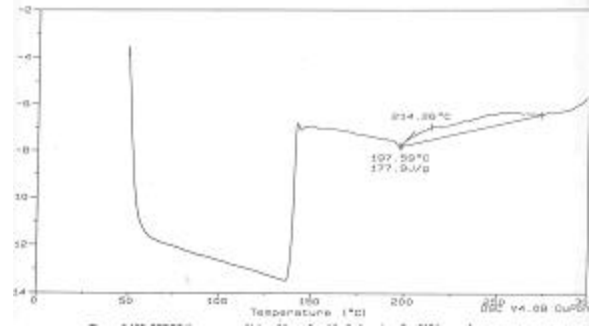


Figure 30: SPDSC thermogram of lube oil from diesel-fuelled engine after 512 hours of usage

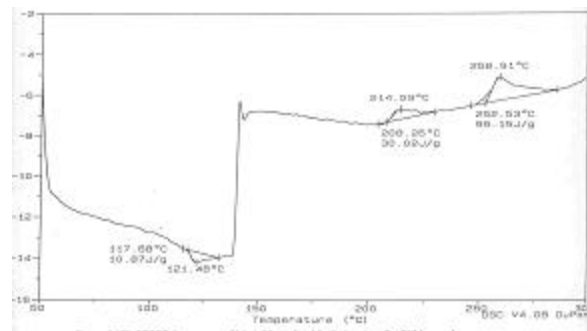


Figure 27: SPDSC thermogram of lube oil from diesel-fuelled engine after 256 hours of usage

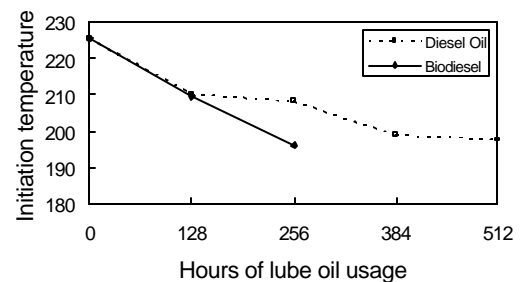


Figure 31: Curve between initiation temperature and hours of lube oil usage

It can be concluded from figure 31, that the oxidation stability of the lubricating oil from biodiesel-operated system is lower than that of diesel-operated system. The presence of oxygen molecule in the molecular structure of LOME present in biodiesel blend may be responsible for lower oxidation instability.

SPDSC studies on remaining samples of biodiesel-fuelled samples could not be conducted because of sudden breakdown of the machine and remote possibility of its repair in near future.

The results of various tribological studies were compared and tabulated in table 3. It was found interesting and encouraging to be noted that biodiesel was performing better in almost all the aspects of performance. The degradation of lubricating oil from diesel engine was compared to oil from biodiesel-operated engine based on these tests.

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
Flash point	↓	↓	15% lower
Moisture content	↑	↑	30% lower
Pentane insoluble		↑	60% lower
Benzene insoluble	↑	↑	50% lower
SPDSC(Oxidation stability)	↓	↓	Slightly higher

Table 3: Tribological investigations summary

From this table, it can be conclusively stated that biodiesel is a definitely superior fuel for use and it not only protects the engine parts from wearing out, but also lubricating oil life is higher. However it is suggested that some changes in the composition of lubricating oil are required, and suitable additives may be added in order to suppress some undesirable properties of the fuel for a dedicated biodiesel operated engine.

Conclusions

Based on the exhaustive engine tests and tribological investigations on the lubricating oils, it can be concluded that biodiesel can be adopted as an alternative fuel for the existing conventional diesel engines without any major modifications in the system hardware. The viscosity of vegetable oil gets drastically reduced after esterification. Esterification has been found to be an effective technique to prevent long-term problems associated with utilisation of vegetable oils such as fuel filter plugging, injector coking, formation of carbon deposits in combustion chamber, ring sticking, and contamination of lubricating oils. Long-term endurance test using biodiesel proved that biodiesel can be used for substituting mineral diesel oil in long run.

Oil analysis studies proved to be a powerful tool to estimate the condition of the engines, and moving parts as well. These tests provide valuable and relevant information on the effect of fuel structure on the lubricating oil system. Comparative studies on various samples of lubricating oil indicated that the density increased with the usage of the lube oil. It was found that the amount of various possible contaminants such as wear debris, soot, resins, oxidation products of oil, presence of moisture was lower in case of biodiesel-fuelled system compared to diesel-fuelled system. Improved performance of biodiesel-fuelled system is due to the self-lubricity properties of the fuel (biodiesel) resulting in lower wear of vital moving parts.

Ash content, which mainly represents wear debris, is found to be lesser in case of biodiesel-fuelled system. Viscosity of the lubricating oil lowered with usage, which is mainly because of fuel dilution. The extent of fuel dilution was significantly lower in the case of biodiesel-operated system. Flash point studies also supported superior performance of biodiesel-operated system. Decrease in flash point is a result of fuel dilution. Pentane and benzene insolubles reflected the extent of wear of moving parts, oil oxidation, and additive depletion. These were found to be lower for biodiesel-operated system reiterating its superior performance.

TLC technique suggested lower ZDDP depletion in the oil samples drawn from biodiesel-operated engine. Ferrographic studies revealed that the wear particle size and quantity was also lower for biodiesel operated engine suggesting additional lubricity properties of the fuel. Sealed pan differential scanning calorimetry tests were carried out to highlight the oxidative stability of the lubricating oil. It was observed that the oxidation stability of lubricating oils from biodiesel-fuelled system was slightly lower than that of lube oil from the diesel-fuelled system.

All these tribological investigations except SPDSC decisively proved that lubricating oil from biodiesel-fuelled system reflected better condition of engine moving parts, indicating thereby the superiority of the new fuel. Based on the studies presented, it is concluded that the fuels of bio-origin are superior in performance to conventional fuels, environment-friendly, biodegradable and do not add to global warming problems. Biodiesel can be readily adopted as a substitute fuel to the existing diesel engines, which are widely used in the rural agricultural sector of the country.

Acknowledgements

The author deeply acknowledge sincere gratitude towards 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. Authors also acknowledge the grant of Senior Research Fellowship by Council for Scientific and Industrial Research, New Delhi, India for conducting research on the above topic.

References

1. Tom Krawczyk, "Biodiesel: alternative fuel makes inroads but hurdles remain", Inform, No.8, Vol. 7, pp. 801-814, 1996.

2. M Devitt, D W Drysdale, I MacGillivray, A J Norris, R Thompson, and J W Twidell, "Biofuel for Transport: an investigation into the viability of rape methyl ester (RME) as an alternative to diesel fuel", *International Journal of Ambient Energy*, No.4, Vol. 14, pp195-218, (1993).
3. Avinash Kumar Agarwal, "Performance Evaluation and Tribological Studies on A Biodiesel Fuelled Compression Ignition Engine" PhD thesis, Center for Energy Studies, IIT, Delhi, August 1999.
4. Avinash Kumar Agarwal, L M Das "Biodiesel Development And Characterization For Use As A Fuel In Compression Ignition Engine", *Journal Of Engineering For Gas Turbine And Power*, (ASME Transaction journal), Vol. 123, pp 440- 447, April 2001.
5. Kelley Fitzpatrick, "Australia Seeks to Hike Oilseed Production", *Inform*, No.8, Vol.7, pp 834-841, 1996.
6. Yusuf Ali and M A Hanna, "Alternative Diesel Fuels from Vegetable Oils", *Bioresource Technology*, 50, pp 153-163, (1994).
7. Kyle W Scholl and Spencer C Sorenson, "Combustion of Soybean Oil Methyl Ester in a Direct Injection Diesel Engine", SAE paper 930934, pp 1450-1461, 1993.
8. D L Van Dyne, J A Weber, C H Braschler, "Macroeconomic Effects of a Community Based Biodiesel Production System", *Bioresource Technology*, Vol.56, pp1-6, 1996.
9. Bernard Freedman, Royden O Butterfield, Everett H Pryde, "Transesterification Kinetics of Soybean Oil", *JAOCS*, Vol. 63, No. 10, October 1986.
10. American Biofuel Association, "Biodiesel: a technology, performance and regulatory overview" Information Resources, Washington DC, 1994
11. Weber J A, Johannes K, "Biodiesel Market Opportunity and Potential Barriers", In Wnditt J S, Gavett E E, Hansen C, Peterson C, Sanderson M A, Shapouri H, and Van Dyne D A (Editors), "Liquid Fuels and Industrial Products from Renewable resources", *Proceedings of the Third fuel conference*, September 15-17, 1996, Nashville TN, ASAE, 1996.
12. M Diasakou, A Louloudi, N Papayannakos, "Kinetics of the Non-Catalytic Transesterification of Soybean Oil", *Fuel*, Vol.77, Issue 12, pp 1297-1302, 1998.
13. George O Dotterer, Walter W Hellmuth, "Differential Infrared Analysis of Engine Oil Chemistry in Sequence V Tests, Road Tests, and Other Laboratory Engine Tests", *Lubrication Engineering*, Vol.41, No.2, pp 89-97, Feb.1985.
14. Han Sheng Lee, Simon S Wang, Donald J Smolenski, "In-Situ Oil Condition Monitoring in Passenger Cars", *Lubrication Engineering*, vol. 50, no. 8, pp 605-611, August 1994.
15. M J Furey, "Film Formation by an Antiwear Additive in an Automotive Engine", *ASLE Transactions*, 2 (1959) 91. 100.
16. I Ming Feng, "Pyrolysis of Zinc-dialkyl-phosphoro-di-thioate and Boundary Lubrication", *Wear*, 3 (1060) pp 309-311.
17. Masuhiko Kawamura, "The Correlation of Antiwear Properties with the Chemical Reactivity of Zinc-dialkyl-di-thio-phosphates", *Wear*, vol. 77. pp 287-294, 1982.
18. Donald J Smolenski, Shirley E, Schwartz Warren, "Automotive Engine-Oil Condition Monitoring", *Lubrication Engineering*, pp716-722, Sept 1994.
19. Y Zhang, P Pei, J M Perez, S M Hsu, "A New Method to Evaluate Deposit forming Tendency of Liquid Lubricants by Differential Scanning Calorimetry" *Lubrication Engineering*, Vol. 48, No. 3. pp 189-195, March 1992.
20. A lamotte, J Auvray, "Utilisation De La Chromatographie Sur Couches Minces Pour L'aanalyse Des Additifs Dand Les Huiles Neuves Et Usagees", *Journal of Chromatography*, Vol. 97, pp 213-222, 1974.
21. E J Ekanem, J A Lori, S A Thomas, "The Determination of Wear Metals in Used Lubricating Oils by Atomic Absorption Spectroscopy Using Sulphanilic Acid as Ashing Agent", *Talanta*, pp 2103-2108, Vol. 44, 1997.
22. Irene M Goncalves, Miguel Murillo, Angela M Gonzalez, "Determination of Metals in Used Lubricating Oils by AAS Using Emulsified Samples", *Talanta*, pp 1033-1042, Vol. 47, 1998.
23. Atsushi Sato, Takashi Oshika, "Electrical Conductivity Method for Evaluation of Oxidative Degradation of Oil Lubricants", *Lubrication Engineering*, Vol. 48 No. 7, pp 539-544, July 1992.
24. J Bijwe, A Garg, and O P Gandhi, "Reassessment of Change of Engine Oil Periodicity in Commercial Vehicles", *Lubrication Engineering*, 1, pp 23-29, 2000.
25. P J Shuff, L J Clarke, "Imaging of Lubricating Oil Insolubles by Electron Microscopy", *Tribology International*, Vol. 24, No.6, pp 381-387, December 1991.
26. James C Fitch, "Oil Analysis and Proactive Maintenance", *The Proactive Maintenance Institute Diagnostics Inc.* 1994.
27. Jayashree Bijwe, Avinash Kumar Agarwal, Atul Sharma, "Assessment of Lubricity of Biodiesel Blends in Reciprocating Wear Mode" SAE Paper 2002-01-2742, SAE Powertrain & Fluid Systems Conference & Exhibition, October 2002, San Diego, CA, USA, 2002.
28. Avinash Kumar Agarwal, Jayashree Bijwe, L M Das "Wear Assessment In Biodiesel Fuelled Compression Ignition Engine" published in the *Proceedings of ASME-ICED 2001 Spring technical conference*, April 2001, Philadelphia, PA.
29. W F Bowman, G W Stachowiak, "Determining The Oxidation Stability of Lubricating Oil Using Sealed Capsule Differential Scanning Calorimetry (SCDSC)", *Tribology International*, Volume 29, No. 1, pp. 27-34, 1986.