A. K. Agarwal

Engine Research Center, University of Wisconsin, Madison 1500 Engineering Drive, Madison, WI 53706 E-mail: avinashagarwal@hotmail.com

L. M. Das

Centre for Energy Studies Indian Institute of Technology, Delhi Hauz Khas, New Delhi-110016, India

Biodiesel Development and Characterization for Use as a Fuel in Compression Ignition Engines

Neat vegetable oils pose some problems when subjected to prolonged usage in CI engine. These problems are attributed to high viscosity, low volatility and polyunsaturated character of the neat vegetable oils. These problems are reduced to minimum by subjecting the vegetable oils to the process of transesterification. Various properties of the biodiesel thus developed are evaluated and compared in relation to that of conventional diesel oil. These tests for biodiesel and diesel oil include density, viscosity, flash point, aniline point/cetane number, calorific value, etc. The prepared biodiesel was then subjected to performance and emission tests in order to evaluate its actual performance, when used as a diesel engine fuel. The data generated for various concentrations of biodiesel blends were compared with base line data generated for neat diesel oil. It was found that 20 percent blend of biodiesel gave the best performance amongst all blends. It gave net advantage of 2.5 percent in peak thermal efficiency and there was substantial reduction in smoke opacity values. This blend was chosen for long term endurance test. The engine operating on optimum biodiesel blend showed substantially improved behavior. A series of engine tests provided adequate and relevant information that the biodiesel can be used as an alternative, environment friendly fuel in existing diesel engines without substantial hardware modification. [DOI: 10.1115/1.1364522]

Introduction

The world is presently confronted with the twin crises of fossil fuel depletion and environmental degradation. Indiscriminate extraction and lavish consumption of fossil fuels have led to reduction in underground based carbon resources. The search for an alternative fuel, which promises a harmonious correlation with sustainable development, energy conservation, management, efficiency and environmental preservation, has become highly pronounced in the present context. For the developing countries of the world, fuels of bio-origin can provide a feasible solution to the crises. The fuels of bio-origin may be alcohol, vegetable oils, biomass, and biogas. Some of these fuels can be used directly while others need to be formulated to bring the relevant properties close to conventional fuels. The power used in the agricultural and transportation sector is essentially based on diesel fuels and it is, therefore, essential that alternatives to diesel fuels be developed. Given the recent widespread use of diesel fuel in various sectors, this study concentrates on assessing the viability of using vegetable oils in the existing diesel engines. Vegetable oils have comparable energy density, cetane number, heat of vaporization, and stoichiometric air/fuel ratio with mineral diesel fuel. The large molecular sizes of the component triglycerides result in the oils having higher viscosity compared with that of mineral diesel fuel. The viscosity of liquid fuels affects the flow properties of the fuel, such as spray atomization, consequent vaporization, and air/fuel mixing. The problem of viscosity has an adverse effect on the combustion of vegetable oils in the existing diesel engines. Besides some problems crop up in the associated fuel pump and injector system. An acceptable alternative fuel for engines has to fulfill the environmental and energy security needs without sacrificing operating performance $[1]$.

Methanol and ethanol are two abundantly available alternative fuels, which possess the potential to be produced from biomass

sources. 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 indirect route of utilizing alcohol as a diesel engine fuel is definitely a superior route as the toxic emissions containing aldehydes are drastically reduced. The problem of corrosion of various engine parts utilizing alcohol as fuel is also solved by way of transesterification $[2]$.

The present work is carried out using a typical vegetable oil by formulating its properties closer to the conventional diesel oil. System design approach has taken care to see that these modified fuels can be utilized in the existing diesel engine without any substantial hardware modifications. India is producing around 6.7×10^6 tons of non-edible oils such as linseed, castor, karanji ~*Pongamia glabra*!, neem ~*Azadirachta indica*!, palash ~*Butea monosperma*), and kusum (*Schlelchera trijuga*). Some of these oils produced even now are not being properly utilized, and it has been estimated that some other plant-based forest derived oils have a much higher production potential. It will be expensive and time consuming to incorporate even a minor design alteration in the system hardware of a large number of existing engines operating in the rural agricultural sector of the country. Keeping this in view, several modes of fuel formulation such as blending, transesterification and emulsification were adopted in the present work to identify the most appropriate mechanism.

Vegetable oils have about 90 percent of the heat content of diesel fuel and they have a favorable output/input ratio of about 2 to 4: 1 for unirrigated crop production. The current prices of vegetable oils in the world are nearly competitive with petroleum fuel price. From amongst the large number of vegetable oils available in the world, if any specific oil needs to be adopted as a continuing energy crop, it is then essential that an oilseed variety having higher productivity and oil content must be produced. Nevertheless, valid technologies must be developed for the use of vegetable oils as an alternative diesel fuel that will permit crop production to proceed in an emergency situation. Vegetable oils in its raw form cannot be used in engines. They have to be converted to a more engine-friendly fuel called biodiesel.

Biodiesel is a chemically modified alternative fuel for diesel

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engines, derived from vegetable oil fatty acids, and animal fat. In its simplest form, the carbon cycle of vegetable oils consist of the fixation of carbon and the release of oxygen by plants through the process of photosynthesis and then combining of oxygen and carbon to form $CO₂$ through processes of combustion or respiration. It is appropriate to mention here that the $CO₂$ released by petroleum diesel was fixed from the atmosphere during the formative years of the earth, whereas the $CO₂$ released by biodiesel gets continuously fixed by plants and may be recycled by the next generation of crops. The carbon cycle time for fixation of $CO₂$ and its release after combustion of biodiesel is quite small as compared (few years) to the cycle time of petroleum oils (few million years). It is well known that petroleum refiners are now facing new sulfur and aromatic compound specifications. Since biodiesel is a fuel made up of esters derived from oils and fats from renewable biological sources, it has been reported to emit far less regulated pollutants than petroleum diesel fuel $[3]$.

Historical Perspective

The inventor of the diesel engine, Rudolf Diesel, in 1885, used vegetable oils (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'' $[4]$. However, higher viscosity is responsible for various undesirable combustion properties of neat vegetable oils. Four well-known techniques are proposed to reduce the viscosity levels of vegetable oils, namely dilution, pyrolysis, micro-emulsion, transesterification [5]. Transesterification, however, is the current method of choice in the study, which results in a fuel very similar to that of diesel oil. 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 monoalcohols 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'' $[6]$.

The process of utilizing biodiesel in the IC engines for transport as well as other applications, is gaining momentum recently. IEA has recognized biodiesel as an alternative fuel for the transportation sector. The European Commission proposed a 12 percent market share for biofuels by the year 2020 [7]. Kaltschmitt et al. conducted a study, which shows that bioenergy carriers offer some clear ecological advantages over fossil fuels such as conserving fossil energy resources or reducing the greenhouse effect $\lceil 8 \rceil$.

Knothe investigated the influence of fatty acid structure on the performance as a diesel fuel [9]. Pischinger et al. found monoesters to be technically attractive in terms of good miscibility with diesel oil, almost similar volumetric heat content, adequate viscosity and cetane number $[10]$. The high carbon residue indicated by the Conradson value and high viscosity are due to the large molecular mass and chemical structure. The high carbon residue is likely to lead to heavy smoke emission from an engine [11].

Hemmerlein et al. established that all of the engines run on rapeseed oil passed the ECE R49 regulation relating to CO, HC, NO_x , and soot emissions in the 13-mode test. the emissions of aromatics, aldehydes, ketones, and particulate matter were higher when rapeseed oil was used. PAH emissions were reduced in larger cylinder IDI engines and elevated in other engine types [12]. Vegetable oil based fuels are biodegradable, non-toxic, and significantly reduce pollution. Reports on the use of biodiesel in diesel engines indicate a substantial reduction in S, CO, PAH, smoke, noise, and particulate emissions $[13–15]$. Furthermore, contribution of biodiesel to greenhouse effect is insignificant, since $CO₂$ emitted during combustion is recycled in the photosynthesis process occurring in the plants and is used as a raw material for biodiesel production $[14,16]$. In 1992, the bi-state development agency (Transit Authority for the Greater St. Louis Metropolitan Area) began a limited 3320 km (2000 mile) test using 30 percent blend of biodiesel and No. 2 diesel fuel in two Ford vans powered by Navistar 7.3 liter engines. They observed that there was no change in the fuel mileage, smoke opacity was reduced by 30 percent, and exhaust odors were less offensive. There were no adverse engine effects. The same study was expanded to include 20 vans and after $41,500$ km $(25,000$ miles), the results were the same [3,17].

In Austria, biodiesel from rapeseed oil is commercialized. The first industrial plant for biodiesel production capacity of 10,000 tons per year in the world went into operation in Austria, in 1991. RME is produced in co-operative and industrial-scale plants. An interesting point is that biodiesel is produced from a mix of RME, SME, and FME (used frying oil methyl ester) in Austria. Tax benefits in Austria and Germany encourage the use of 100 percent biodiesel fuel in ecologically sensitive areas and agricultural and mountainous region [18,19]. In Ireland, two pilot projects on the use of biodiesel (RME) in commercial vehicles are reported. In the first project, pure biodiesel was used in buses, trucks, and in pleasure cruisers. The RME used was obtained through oil extraction followed by esterification on a small-scale tractor-mounted esterification unit. The second project involved a comparative analysis of the behavior of a number of vehicles operated on RME and SME, imported from UK and Italy, respectively. Vehicle testing started in mid-1996. A principal disadvantage of rape oilseed as a source of biodiesel in Ireland was its economic feasibility, as it is up to 0.25 ECU/liter (about 6.6 ECU/GJ) more expensive than its fossil-based equivalent. In Denmark, two companies produced non-food rapeseed oil, on a commercial basis, for export. At present, there is no commercial production of biodiesel in Denmark. During a test, four city buses were running on biodiesel for 3 months. The results were promising but not satisfactory from environmental point of view. The Danish National Transport Plan ''Trafik 2000'' mentions the use of biofuels as one out of five major instruments to be used to reduce $CO₂$ emissions from the transport sector. However, there is no commitment for large-scale use within the government $[20]$. In the United States, fuel tax assistance or other governmental aid or regulations could propel biodiesel into a high volume, lower cost production track that enables it to compete head-to-head with diesel fuel for a variety of applications $[4]$.

Vegetable Oil and Diesel Fuel: A Comparison

The ideal diesel fuel molecules are saturated non-branched hydrocarbon molecules with carbon number ranging between 12 to 18 whereas vegetable oil molecules are triglycerides generally with no branched chains of different lengths and different degrees of saturation. It may be noticed that vegetable oils contain a substantial amount of oxygen in their molecular structure. Fuel properties for the combustion analysis of vegetable oils can be grouped conveniently into physical, chemical, and thermal properties. Physical properties include viscosity, density, cloud point, pour point, flash point, boiling range, freezing point, and refractive index. Chemical properties comprise chemical structure, acid value, saponification value, iodine value, peroxide value, hydroxyl value, acetyl value, overall heating value, ash and sulfur contents, sulfur and copper corrosions, water and sediment residues, oxidation resistance, ignitability and thermal degradation products. The thermal properties are distillation temperature, thermal degradation point, carbon residue, specific heating content, and thermal conductivity.

American society of testing methods (ASTM) has prescribed certain tests and their limits for diesel fuel to be used in CI engines. For any alternative fuel to be suitable for long-term engine operation without engine modifications, it should be in conformity or within close range to these ASTM limits $[21]$.

The characteristics of the variety of available vegetable oils fall within a fairly narrow band and are close to those of diesel oil. Vegetable oils have about 10 percent less heating value than diesel oil due to the oxygen content in their molecules. The kinematic viscosity is, however, several times higher than that of diesel oil. The high viscosity, 35–45 cSt as against about 4.0 cSt for diesel oil at 40°C, leads to problems in pumping and atomization in the injection system of a diesel engine. The high carbon residue indicated by the conradson value and high viscosity are due to the large molecular mass and chemical structure. The high carbon residue is responsible for heavy smoke emission from an engine. Vegetable oils have poor volatility characteristics, prohibiting their use in SI engines. Vegetable oils are suitable as fuels only for CI engines. The cetane number of most of the vegetable oils fall in the range $35-40$, which is short of the minimum cetane number of 40 required for diesel engine fuel.

Since neat vegetable oils are not suitable as fuels for a diesel engine, they have to be modified to bring their combustion-related properties closer to those of diesel oil. This fuel modification is mainly aimed at reducing the viscosity to get rid of flow related problems. The methods employed include the heating of vegetable oil, thermal cracking of the highly complex vegetable oil molecule into lighter ones, and transesterification, in which methanol/ ethanol substitutes glycerol, splitting the vegetable molecule into three lighter molecules. Vegetable oils have larger molecules, up to four times larger than typical diesel fuel molecules. The high molecular weights of vegetable oils result in low volatility as compared to diesel fuel, which leads to the oils sticking to the injector or cylinder walls [4]. Oils then undergo oxidative and thermal polymerization, causing a deposition on the injector, forming a film that continues to trap fuel and interfere with combustion and leads to more deposit formation, carbonization of injector tips, ring sticking, and lubricating oil dilution and degradation. The accompanying inefficient mixing with air contributes to incomplete combustion. The combination of high viscosity and low volatility of vegetable oils causes poor cold engine start-up, misfire, and ignition delay.

A host of plant and forest resources are available in the world from which different vegetable oils can be produced and formulated for use in diesel engines. The present work has been carried with such an objective, where a non-edible oil has been appropriately modified by way of esterification and subsequently used for running the diesel engine.

Linseed oil was selected for the present investigation, as it is available in large quantities and non-edible in nature. Linseed oil is obtained from the dried ripe seed of the flex plant, *Linum usitaissimum*, grown in the temperate areas of the world. Its viscosity is lower than most of other vegetable oils. It has high linoleic acid content. Linoleic acid is a straight chain molecule of 18 carbon atoms $[C_{17}H_{29}COOH]$ with three double bonds at 9-10, 12-13, and 15-16 carbons. Its high degree of unsaturation is responsible for the drying properties of the oil. Linseed oil has lower heating value (LHV) of 39.75 MJ/kg (dry). The comparison of the properties of linseed oil and diesel oil is given in Table 1.

Engine System

Nearly all agricultural tractors, pump sets, farm machinery, and transport vehicles have DI diesel engines. With a view of introducing biodiesel to such systems, it is appropriate to mention here that if these engines run over long periods with vegetable oils, or mixtures of diesel fuel with a high content of unmodified vegetable oils, deposits get formed on several engine parts, which

Table 1 Comparison of properties of linseed oil with diesel oil †**9**‡

Properties	Diesel oil	Linseed oil
Specific gravity	0.835	0.935
Net calorific value (MJ/Kg)	45.158	39.75
Kinematic viscosity at 37.8°C (cSt)	3.9	29.3
Color	Light brown	Pale yellow
Stoichiometric air fuel ratio	14.9	12.08

subsequently cause problems in fuel spray. Engines do not take up high load level, even after a few hundred hours and at last, the engine fails catastrophically.

Keeping the specific features of diesel engines in mind, a typical engine system widely used in the agricultural sector in developing countries, has been selected for the present experimental investigation. This is a single cylinder, direct injection, watercooled, portable diesel engine of 4 kW rating with an alternator coupled to it. The engine was provided with suitable arrangements, which permitted wide variation of controlling parameters. This unit, manufactured by Perry & Co., India, is a compact, portable captive 4 kW gen-set run by diesel fuel. It is widely used mostly for agricultural purposes and in many small and medium scale commercial purposes. This is a single cylinder, four-stroke, vertical, water-cooled system having a bore of 85 mm and a stroke of 110 mm. At the rated speed of 1500 rpm, the engine develops 4 kW power output in pure diesel mode. The engine can be started by hand cranking, using decompression lever. The engine is provided with a centrifugal speed governor. The compression ratio is 16.7. The inlet valve opens 4.5 deg BTDC and closes 35.5 deg ABDC. The exhaust valve opens 35.5 deg BBDC and closes 4.5 deg ATDC. The test engine is directly coupled to a 220 V, single phase ac generator of sufficient capacity to absorb the maximum power produced by the engine.

Esterification Process

The use of biodiesel fuel is an effective way of substituting diesel fuel in the long run. One important conclusion that can be drawn from the work done earlier in our laboratory is that vegetable oils as fuel cannot be used directly in the engine. Several problems crop up if the unmodified fuel is used and viscosity is the major offender. It has been observed that esterification is a very effective way to modify the vegetable oil structure and reduce its viscosity. If vegetable oil processing costs can be reduced through increased plant capacities, it would become an economically viable alternative to diesel fuel.

The formation of methyl esters by transesterification of vegetable oils requires three moles of alcohol stoichiometrically. However, transesterification is an equilibrium reaction in which excess alcohol is required to drive the reaction close to completion. Fortunately, the equilibrium constant favors the methyl esters such that only a 5:1 molar ratio of methanol: triglyceride is sufficient for a 95 percent–98 percent yield of ester. It might be anticipated that in such an equilibrium system, the observed phaseseparation of the by-product, glycerol would play a major role in achieving conversions close to 100 percent. Various catalysts were tried for the process of transesterification by several earlier researchers, e.g., magnesium and calcium oxides and carbonates, basic and acidic macro-reticular organic resins, alkaline alumina, phase transfer catalysts, sulfuric acid, P-toluenesulphonic acid, and dehydrating agents as cocatalysts [22]. Catalysts reported to be effective at room temperature were alkoxides and hydroxides. The chemical reaction of the transesterification process is shown

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below.

 $R¹$, $R²$, $R³$ and $R⁴$ represent various alkyl groups [23]. For methanolysis, two distinct phases are present as the solubility of the oil in the methanol is low. The reaction mixture was stirred vigorously. Optimum reaction conditions for the maximum yield of methyl esters were found to be 0.8 percent (based on weight of oil) sodium methoxide catalyst and 67 percent excess methanol at room temperature for 2.5 hours. Glycerol phase separation was very small or did not occur when less than 67 percent of the theoretical amount of methanol was used. There are some alternative methods available for the process of esterification. An alternative reactive substance is sodium hydroxide (NaOH), which is cheaper but it requires a higher reaction temperature $(70^{\circ}$ C) and produces a useless by-product. As far as KOH is concerned, it reacts at room temperature and the by-product, potassium sulfate, can be sold as a fertilizer. Methanol is then removed by distillation to raise the flash point of the ester produced. All traces of methanol, KOH, free fatty acids (FFA), chlorophyll, etc., go into the glycerin phase. Glycerin is processed in two stages. The first stage glycerin of 90 percent–95 percent purity is further esterified to 98 percent purity in the second stage. The transesterification plant requires 50 kW per ton of ester produced. Energy required in production of glycerin accounts for 60 percent–70 percent of the total energy used.

The molecular weight of linoleic acid $(C_{17}H_{28}COOH)$ in linseed oil molecule is 278. This is also confirmed by the CHNO analysis and infrared spectroscopy. The molecular weight of methanol (CH₃OH) is 32. Linseed oil contains 9.40 percent $(18:0)$ saturated linoleic acid, 20.2 percent $(18:1)$ unsaturated linoleic acid, 12.7 percent $(18:2)$ unsaturated linoleic acid, 53.3 percent $(18:3)$ unsaturated linoleic acid. Thus linseed oil contains 95.6 percent total linoleic acid $[24]$. The density of linseed oil is 0.935 and methanol is 0.80. Every liter of linseed oil requires 643 ml of methanol. For esterification in laboratory, 2 liters of linseed oil was heated up to 70°C in a round bottom flask. 16 g of KOH was dissolved in 1286 ml of methanol in a separate vessel, which was poured into round bottom flask while stirring the mixture continuously using constant stirring mechanism. The mixture was stirred and maintained at 70°C for 1 h and then allowed to settle under gravity in a separating funnel. About 2.3 liter of ester separated from 230 ml glycerol and formed the upper layer in the separating funnel. The separated ester was mixed with 250 ml of hot water and allowed to settle under gravity for 24 h. The catalyst got dissolved in water, which was separated. Moisture was removed from this purified ester using silica gel crystals. The ester was then blended with petroleum diesel oil in various concentrations for preparing biodiesel blends to be used in CI engine for conducting various engine tests. The level of blending, for convenience is referred as Bxx. The xx indicates the amount of biodiesel in percentage in the blend (i.e., a B20 blend is 20 percent biodiesel and 80 percent diesel oil) $[25]$.

Biodiesel Characterization

Several tests were conducted to characterize biodiesel in relation to diesel oil in order to evaluate various physical, chemical, and thermal properties such as density, API gravity, viscosity

Table 2 Various characterization properties of biodiesel and diesel

Properties	ASTM Test No.	Linseed oil	Diesel Oil	LOME Biodiesel	20% biodiesel blend
Density		0.935	0.855	0.874	0.859
API gravity	---	19.833	33.997	30.399	33.226
Viscosity (40°C)	D445	23.93	3.06	3.59	3.20
Viscosity (100°C)	D445	6.00	1.05	1.16	1.32
Flash point (°C)	D93	186	76	172	128
Pour point $(^{\circ}C)$	---	---	-16	-15	-16
Aniline Point (°C)	---		69	83	73
Diesel Index	---		53.10	55.14	54.29
Cetane number			50	52	51
Sulfur (ppm)	D ₁₂₉		2500	50	2000
Ash Content (%)	D482		0.01	0.002	0.008
Calorific Value (KJ/Kg)			43,800	40.374	43,200

 $(40^{\circ}$ C and 100° C), flash point, pour point, aniline point, cetane number, calorific value, etc. The results obtained are shown in Table 2.

The process of esterification brings about a drastic change in the density of linseed oil and the LOME; i.e., neat biodiesel has almost similar density to that of diesel. Neat biodiesel was miscible in any proportion with that of mineral diesel oil. The optimized blend of biodiesel has density very close of diesel oil.

Linseed oil has a higher viscosity at 40°C compared to diesel oil. This property of linseed oil makes it unsuitable for direct use in CI engines. By converting linseed oil into its methyl esters, the viscosity comes down closer to diesel oil. The diesel oil viscosity is normally between 3 and 4 cSt at 40°C and it varies depending upon its constituents. Thus fuel oil, which has viscosity within this range, does not pose any handling problems to the fuel handling systems in the existing diesel engines. Hence, no hardware modifications are required for handling this fuel in the existing system. The viscosity at 100°C of biodiesel also closely follows diesel oil. This property makes it suitable for fuel use in the existing engine systems.

The flash point of linseed oil was lowered after transesterification but it was still higher than diesel oil. Fuels with flash point above 66°C are regarded as safe. Thus, biodiesel is an extremely safe fuel to handle compared to diesel oil. Even 20 percent biodiesel blend has a flash point much above that of diesel oil, making it a preferable choice as far as safety is concerned. Pour point is a criterion used for low temperature performance of the fuels. Pour point analysis results suggest that the performance of biodiesel is as good as diesel oil in cold surroundings.

Cetane number of biodiesel fuel was evaluated using an alternative chemical method. This method (aniline point method) was first tested for determining the cetane number of diesel fuel, whose cetane number was already known. The cetane number evaluated by this method and the cetane number given by the fuel supplier matched and this established the precision of the method. Then this method was applied to determine cetane number of biodiesel fuel. In this method, aniline is used as a reagent to evaluate aniline points for these fuels. Diesel index is calculated using aniline point and API gravity. The calculated values of diesel index are given in the table. The diesel index is three units higher than cetane number. These results reveal that biodiesel has a higher cetane number than petroleum diesel oil. Even 20 percent blend of biodiesel showed improvement in cetane number. Thus, biodiesel is an attractive fuel by combustion and knocking point of view and it can be used as a cetane point improver. Even lower concentrations in the range of 3 percent–5 percent of biodiesel blended with diesel are found to improve cetane number of diesel oil by various researchers.

Benzoic acid was used as a reference fuel to determine the calorific value of biodiesel and linseed oil. The results of the tests

conducted on various fuels using Bomb calorimeter are given in Table 2. The residue left after combustion of diesel oil in the crucible was in the form of black carbon ash pellets (charcoal like foamy substance). The quantity of such a foamy charcoal like ash substance was very low in case of LOME combustion. This typical observation points out lesser ash content and cleaner combustion characteristics of LOME. This fact was subsequently supported by the engine emission tests.

Engine Tests

A series of exhaustive engine tests were carried out on CI engine using diesel and biodiesel blends separately as fuels at 1500 RPM. The experimental data generated were calculated, presented through appropriate graphs. Performance and emission test was conducted on various biodiesel blends in order to optimize the blend concentration for long term usage in CI engines. This test was carried out on an engine, which has already been subjected to preliminary run-in. This test is aimed at optimizing the concentration of ester in the biodiesel blends to be used for long term engine operation. To achieve this, several blends of varying concentrations were prepared ranging from 0 percent (Neat diesel oil) to 100 percent (Neat biodiesel) through 5 percent, 10 percent, 15 percent, 20 percent, 25 percent, 30 percent, 40 percent, 50 percent, 75 percent. These blends were then subjected to performance and emission tests on the engine. The performance data was then analyzed from the graphs recording power output, torque, specific fuel consumption, and smoke density for all the blends of biodiesel. The optimum blend was found out from the graphs based on maximum thermal efficiency and smoke opacity considerations.

The major pollutants appearing in the exhaust of a diesel engine are smoke and the oxides of nitrogen. For measuring the smoke opacity, Hartridge Exhaust smoke-meter (model No. APM 700 M), was used. Hartridge smoke meter consists of two identical tubes, a smoke type and a clean air tube. A pressure relieve valve allows a regulated quantity of exhaust through the smoke tube. During smoke density measurements, a light source $(45-W$ bulb) at one end of the smoke tube projects a light beam through smoke, which at the other end falls on a photoelectric cell. Clean air tube is used for initial zero setting. Of the light beam projected across a flowing stream of exhaust gases, a certain portion of light is absorbed or scattered by the suspended soot particles in the exhaust. The remaining portion of the light falls on a photocell, generating a photoelectric current, which is a measure of smoke density. A micro-voltmeter is connected to the photoelectric cell with its scale graduated 0–100, indicating the light absorbed in Hartridge Smoke Meter unit. Zero reading corresponds to no smoke (clean air), whereas 100 reading refers to dense smoke, which allows no light to pass through $[26]$.

The brake specific fuel consumption is not a very reliable parameter to compare the two fuels as the calorific value and the density of the blend follow a slightly different trend. Hence brake specific energy consumption is a more reliable parameter for comparison. However this parameter is also compared in the present study to compare volumetric consumption of the two fuels. For an optimum biodiesel system, the blend concentration has been determined based on the following performance and emissionrelated parameters.

Maximum thermal efficiency at all loads Minimum brake specific energy consumption Better smoke opacity values Lower frictional horsepower

Based on these parameters, the curves were compared to base-line diesel curve in two separate groups in order to optimize blend concentration. In the first group, lower concentrations up to 25 percent were compared with that of diesel oil and in the second group, higher concentrations from 30 percent to 100 percent were compared to that of base-line data.

Fig. 1 Comparison of thermal efficiency vs. BMEP curves for lower concentrations of biodiesel

Comparison for Lower Blend Concentrations

The various characteristic curves for lower concentrations of biodiesel blend are compared in Figs. 1–4.

Comparison for Higher Concentration Blends

The various characteristic curves for higher concentrations of biodiesel blend are compared in Figs. 5–8.

The trend of the thermal efficiency curves $(Fig. 1$ and Fig. 5) has generally improved by mixing biodiesel in mineral diesel oil. The thermal efficiency of the engine is found to improve by increasing concentration of biodiesel in the blend. The possible reasons may be more complete combustion, and additional lubricity of biodiesel hence, with increasing amount of biodiesel, the frictional horsepower losses in the engine follow a declining trend. Additional experiments were conducted to determine the additional lubricity aspect of biodiesel fuels. A series of experiments were conducted to compare lubricity of various concentrations of LOME in biodiesel blends. These long duration non-engine tests were conducted employing reciprocating motion in SRV optimol wear tester in order to evaluate the coefficient of friction, specific

Fig. 2 Comparison of BSFC vs. BMEP curves for lower concentrations of biodiesel blend

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Fig. 3 Comparison of smoke opacity vs. BMEP curves for lower concentrations of biodiesel blend

wear rates etc. The extent of the damage, coefficient of friction and specific wear rates were found to decrease with increase in percentages of LOME in the biodiesel blend $[27]$. These tests on SRV optimol wear tester for quantification of lubricity reflected that the biodiesel lubricating fluids show lower coefficient of friction hence lower frictional losses in diesel engines.

This reduction in frictional losses is also reflected by the decreasing trend followed by unaccounted losses, which can be noticed from the heat balance sheets for various concentrations. The energy saved by decrease in frictional horse-power makes additional contributions towards useful energy, cooling losses, and exhaust losses. This reflects in increased thermal efficiency, cooling losses and exhaust losses. It is evident from the graphs of exhaust temperature vs. BMEP (Fig. 4 and Fig. 8) that the exhaust gas temperature is also increasing along with thermal efficiency as a function of blend concentration initially. Smoke opacity for biodiesel blends (Fig. 3 and Fig. 7) is also noticed to be generally lower than that of diesel oil. It also repeats the trend followed by thermal efficiency curves. There are two main reasons: the higher

Fig. 5 Comparison of thermal efficiency vs. BMEP curves for higher concentrations of biodiesel blend

thermal efficiency means, better and complete combustion and lesser amount of unburned hydrocarbons in the engine exhaust thus improving smoke opacity values.

The molecule of biodiesel, i.e., LOME, contains some amount of oxygen that takes part in combustion and this may be a possible reason for more complete combustion. The oxygen molecule present in biodiesel molecular structure may be readily available for oxygen. However, it was noticed that after a certain limit of biodiesel concentration, the thermal efficiency trend is reversed and it starts decreasing. This behavior of biodiesel fuel needs advanced investigations.

An important observation is that all the blends have a higher thermal efficiency than the baseline data of diesel fuel. A graph between the concentration of ester blend and improvement in peak thermal efficiency for various concentrations of biodiesel blend is plotted in Fig. 9.

This graph reflects that ester blend with concentration of 20 percent gave maximum improvement in peak thermal efficiency. These observations were taken six times and there was hardly any difference in the values of the performance and emission parameters calculated. However, in order to minimize any experimental inaccuracies that might have got in, the average of the six readings

Fig. 4 Comparison of exhaust temperatures vs. BMEP curves for lower concentrations of biodiesel

Fig. 6 Comparison of BSFC vs. BMEP curves for higher concentration of biodiesel blend

Fig. 7 Comparison of smoke opacity vs. BMEP curves for higher concentrations of biodiesel blend

Fig. 8 Comparison of smoke temperature vs. BMEP curves for higher concentrations of biodiesel blend

Fig. 9 Improvement in peak thermal efficiency vs. concentration of biodiesel blend curve

Oxides of nitrogen (ppm) 1200 \cdot Desa Oi 20%Biodese 800 400 0 \overline{c} 3 5 $\mathbf 0$ 4 6 $\overline{7}$ 1 $BMP(10⁴)$ M \hat{f}

Fig. 10 Concentration of oxides of nitrogen vs. BMEP

were used for calculations. This blend of 20 percent also gave minimum brake specific energy consumption and minimum smoke opacity. Hence this blend was selected as the optimum blend for further investigations and long-term engine operations. Long-term endurance test was conducted with 20 percent biodiesel blend and diesel oil on two similar engines. For diesel fuel, the most important pollutants are smoke and NO*^x* hence the optimum biodiesel concentration is also subjected to evaluation of NO*^x* emissions.

From the NO_x curves given in Fig. 10, two important observations were made. First, NO*^x* emissions are a direct function of engine loading. This is expected because with increasing load, the temperature of the combustion chamber increases and NO*^x* formation is a strongly temperature dependent phenomenon. Second important observation is that the NO*^x* emissions in the case of biodiesel fuel are higher by approximately 5 percent. These higher NO_x emissions may be due to higher temperatures of the combustion chamber using biodiesel. This is also evident from higher exhaust temperatures from the biodiesel-fueled engine.

The NO_x emissions from B20 fueled diesel engines were found to be 2 percent higher than conventional diesel oil according to a report on biodiesel from National Biodiesel Board of US [1]. In our study, 20 percent biodiesel blend gave 5 percent higher NO*^x* emissions. This difference may be because of difference in engine geometry and compression ratio. The B20 is also reported to provide additional lubricity compared to conventional fuels and demonstrate similar fuel consumption, horsepower and torque, as petroleum fuel [1]. The present study also demonstrated similar results and is in full agreement with the findings of these researchers.

The long-term endurance test for constant speed engines was performed after the performance tests were carried out as specified in the Indian Standard Code ''IS: 10000, part VIII-1980,'' ''Methods of tests for internal combustion engines: Part VIII Performance tests.'' After the completion of performance tests, two similar engines were operated using two different fuels for 32 cycles (each of 16 h continuous running) at rated speed. The test cycle followed is specified in the Table 3 [25].

At the end of each 16-h cycle, both the engines were stopped for necessary servicing, and minor adjustments were carried out in accordance with the manufacturer's schedule, e.g., tappet settings,

Table 3 Test cycle for long-term endurance test

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

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and make up oil addition. The amounts of make up oil used during the test were used to establish the lubricating oil consumption rate. The lubricating oil samples were collected from the engines after every 128 h for conducting various tribological studies.

The long-term endurance test suggested that biodiesel fuel does not have any adverse effect on wear of various vital moving parts of the engine. The problems which were present in long term operation of using unmodified vegetable oils as fuel such as injector coking, lube oil dilution, carbon deposits on piston, ring sticking, fuel pump failure, catastrophic failure of the engine were found to have been completely eliminated.

The pure LOME cost 50 percent higher than diesel oil in India hence 20 percent biodiesel blend costs about 10 percent more expensive. This work is carried out only on linseed oil but this work can be extended to a host of vegetable oil available from agricultural and forest resources.

Conclusions

Based on the exhaustive engine tests, it can be concluded that biodiesel can be adopted as an alternative fuel for the existing conventional diesel engines without any major modifications required in the system hardware.

Esterification is a process, which brings about a change in the molecular structure of the vegetable oil molecules, thus bringing down the levels of viscosity and unsaturation of vegetable oils. The viscosity of vegetable oil reduces substantially after esterification. The density and viscosity of the linseed oil methyl ester formed after esterification were found to be very close to petroleum diesel oil. The flash point of LOME was higher than that of diesel oil. The 20 percent biodiesel blend also demonstrated comparatively higher flash point than petroleum diesel oil and was in range of 'safe fuel'. The cetane number for the neat diesel oil obtained by this method is 50 and cetane number of LOME was 52. A 20 percent blending of LOME with diesel oil improved the cetane number of diesel oil. Lower concentrations of LOME in biodiesel blends can be used as a cetane improver. The calorific value of LOME was found to be slightly lower than petroleum diesel oil. All these tests for characterization of biodiesel oil demonstrated that almost all the important properties of biodiesel are in very close agreement with the diesel oil making it a potential candidate for the application in compression ignition engines for partial replacement of diesel fuel.

A diesel engine can perform satisfactorily on biodiesel fuel without any engine hardware modifications. Long-term endurance test using biodiesel proved that biodiesel can be used for substituting mineral diesel oil in long run. The 20 percent biodiesel blend was found to be the optimum concentration for biodiesel blend, which improved the thermal efficiency of the engine by 2.5 percent, reduced the exhaust emissions and the brake specific energy consumption. Smoke emissions also reduced appreciably. The higher the concentration of biodiesel blend, higher was the reduction in exhaust smoke levels. Exhaust temperatures increased as a function of the concentration of biodiesel blend, i.e., higher the percentage of LOME; higher were the exhaust temperatures. Increase in the exhaust temperature of a biodiesel-fueled engine led to approximately 5 percent increase in NO*^x* emissions for 20 percent biodiesel blend. This is so because NO*^x* formation is a highly temperature dependent phenomenon.

Esterification has been found to be an effective technique to prevent some long-term problems associated with utilization of vegetable oils such as fuel filter plugging, injector coking, formation of carbon deposits in combustion chamber, ring sticking, and contamination of lubricating oils. The carbon deposits on piston top and injector coking substantially reduced in biodiesel-fueled system. The performance of biodiesel-fueled engine was marginally better than the diesel-fueled engine in terms of thermal efficiency, brake specific energy consumption, smoke opacity, wear of vital components, and exhaust emissions for entire range of operations. It was conclusively proved that self-lubricity of LOME in biodiesel played a key role in engine performance. Biodiesel is proved to be a potential candidate for partial substitute of mineral diesel oil.

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