

Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines

Avinash Kumar Agarwal*

Department of Mechanical Engineering, Indian Institute of Technology Kanpur, Kanpur-208 016, India

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Abstract

The increasing industrialization and motorization of the world has led to a steep rise for the demand of petroleum-based fuels. Petroleum-based fuels are obtained from limited reserves. These finite reserves are highly concentrated in certain regions of the world. Therefore, those countries not having these resources are facing energy/foreign exchange crisis, mainly due to the import of crude petroleum. Hence, it is necessary to look for alternative fuels which can be produced from resources available locally within the country such as alcohol, biodiesel, vegetable oils etc. This paper reviews the production, characterization and current statuses of vegetable oil and biodiesel as well as the experimental research work carried out in various countries. This paper touches upon well-to-wheel greenhouse gas emissions, well-to-wheel efficiencies, fuel versatility, infrastructure, availability, economics, engine performance and emissions, effect on wear, lubricating oil etc.

Ethanol is also an attractive alternative fuel because it is a renewable bio-based resource and it is oxygenated, thereby providing the potential to reduce particulate emissions in compression-ignition engines. In this review, the properties and specifications of ethanol blended with diesel and gasoline fuel are also discussed. Special emphasis is placed on the factors critical to the potential commercial use of these blends. The effect of the fuel on engine performance and emissions (SI as well as compression ignition (CI) engines), and material compatibility is also considered.

Biodiesel is methyl or ethyl ester of fatty acid made from virgin or used vegetable oils (both edible and non-edible) and animal fat. The main resources for biodiesel production can be non-edible oils obtained from plant species such as *Jatropha curcas* (Ratanjyot), *Pongamia pinnata* (Karanj), *Calophyllum inophyllum* (Nagchampa), *Hevea brasiliensis* (Rubber) etc. Biodiesel can be blended in any proportion with mineral diesel to create a biodiesel blend or can be used in its pure form. Just like petroleum diesel, biodiesel operates in compression ignition (diesel) engine, and essentially require very little or no engine modifications because biodiesel has properties similar to mineral diesel. It can be stored just like mineral diesel and hence does not require separate infrastructure. The use of biodiesel in conventional diesel engines result in substantial reduction in emission of unburned hydrocarbons, carbon monoxide and particulate. This review focuses on performance and emission of biodiesel in CI engines, combustion analysis, wear performance on long-term engine usage, and economic feasibility.

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Keywords: Biofuels; Alcohol; Biodiesel; Performance and emissions; Combustion analysis; Tribology; Wear analysis

*Tel.: +91 512 2597982; fax: +91 512 259 7408.

E-mail address: akag@iitk.ac.in.

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1. 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

alternative fuels, which promise a harmonious correlation with sustainable development, energy conservation, efficiency and environmental preservation, has become highly pronounced in the present context.

The fuels of bio-origin can provide a feasible solution to this worldwide petroleum crisis. Gasoline and diesel-driven automobiles are the major sources

of greenhouse gases (GHG) emission [1–3]. Scientists around the world have explored several alternative energy resources, which have the potential to quench the ever-increasing energy thirst of today's population. Various biofuel energy resources explored include biomass, biogas [4], primary alcohols, vegetable oils, biodiesel, etc. These alternative energy resources are largely environment-friendly but they need to be evaluated on case-to-case basis for their advantages, disadvantages and specific applications. Some of these fuels can be used directly while others need to be formulated to bring the relevant properties closer to conventional fuels. Due to the recent widespread use of petroleum fuels in various sectors, this study concentrates on assessing the viability of using alternative fuels in the existing internal combustion engines.

The present energy scenario has stimulated active research interest in non-petroleum, renewable, and non-polluting fuels. The world reserves of primary energy and raw materials are, obviously, limited. According to an estimate, the reserves will last for 218 years for coal, 41 years for oil, and 63 years for natural gas, under a business-as-usual scenario [1,5,6]. The enormous growth of world population, increased technical development, and standard of living in the industrial nations has led to this intricate situation in the field of energy supply and demand. The prices of crude oil keep rising and fluctuating on a daily basis. The crude oil prices are at near record levels and are stabilizing at about US\$65 per barrel now. The variations in the energy prices over last decade are shown in Fig. 1. This necessitates developing and commercializing fossil-fuel alternatives from bio-origin. This may well be the main reason behind the growing awareness and interest for unconventional bio energy sources and

fuels in various developing countries, which are striving hard to offset the oil monopoly.

1.1. Environmental and health implications of pollutants

Environmental concerns have increased significantly in the world over the past decade, particularly after the Earth Summit '92. Excessive use of fossil fuels has led to global environmental degradation effects such as greenhouse effect, acid rain, ozone depletion, climate change, etc. There is a growing realization worldwide that something constructive has to be done soon to reduce the GHG emissions. In the Kyoto conference on global climate change, nations world over have committed to reduce GHG emissions significantly.

Use of various fossil fuels such as petroleum products and coal lead to several environmental problems such as reduction in underground-based carbon energy sources, serious modifications in earth's surface layer, subsidence of ground surface after extraction of fuels and minerals etc. Usage of these fossil fuels has led to increase in CO₂ levels in atmosphere from 280 PPM in pre-industrial era to 350 PPM now. These CO₂ levels are still climbing as a function of fuel burnt leading to greenhouse effect, acid rains, smog and change of climate world-over. These environmental implications are being felt in day-to-day life in the form of changing weather patterns, more severe winters and summer globally, foggy conditions in several parts of the world for a prolonged period during winter months. The combustion of fossil fuel has an adverse affect on human health through increased air pollution in cities, acid rains, build up of carbon dioxide, changing heat balance of the earth, etc. In fact, projections for the 30-year period from 1990 to 2020 [8–10] indicate that vehicle travel, and consequently fossil-fuel demand, will almost triple and the resulting emissions will pose a serious problem. The main reason for increased pollution levels, in spite of the stringent emission norms that have been enforced, is the increased demand for energy in all sectors and, most significantly the increased use of automobiles. The global population of motor vehicles on the roads today is half a billion, which is more than 10 times higher than what was in 1950.

Combustion of various fossil fuels leads to emission of several pollutants, which are categorized as regulated and unregulated pollutants. Regulated pollutants are the ones, whose limits have been

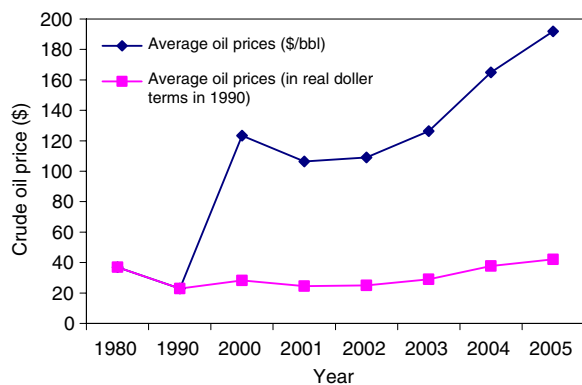


Fig. 1. Crude oil prices [7].

prescribed by environmental legislations (such as USEPA, EURO and Bharat norms) whereas there are some pollutants for which no legislative limits have been prescribed. These are categorized as unregulated pollutants. Regulated pollutants include NO_x , CO, HC, particulate matter (PM) and unregulated pollutants include formaldehyde, benzene, toluene, xylene (BTX), aldehydes, SO_2 , CO_2 , methane etc. [11–13].

These regulated as well as unregulated pollutants contribute to several harmful effects on human health, which are further categorized as short- and long-term health effects. The short-term health effects are caused by CO, nitrogen oxides, PM, (primarily regulated pollutants) formaldehyde etc., while long-term health effects are caused mainly by poly-aromatic hydrocarbons (PAH's), BTX, formaldehyde, (primarily unregulated pollutants) etc. CO is fatal in large dosage, aggravates heart disorders, affects central nervous system, and impairs oxygen-carrying capacity of blood by forming carboxy-hemoglobin. Nitrogen oxides cause irritation in respiratory tract. HC's cause drowsiness, eye irritation, and coughing [14–16].

These pollutants also contribute towards several regional and global environmental effects. Regional environmental effects such as summer smog are because of aldehydes, carbon monoxides, nitrogen oxides etc. Winter smog is because of particulate. Acidification is caused by nitrogen oxides, sulfuric oxides etc. Several global effects like ozone layer depletion, global warming etc. are caused by CO_2 , CO, methane, non-methane hydrocarbons, nitrogen oxides etc. [17,18].

1.2. Biofuels for transportation sector

Transportation and agricultural sector is one of the major consumers of fossil fuels and biggest contributor to environmental pollution, which can be reduced by replacing mineral-based fuels by bio-origin renewable fuels. There are a variety of biofuels potentially available, but the main biofuels being considered globally are biodiesel and bio-ethanol. Bio-ethanol can be produced from a number of crops including sugarcane, corn (maze), wheat and sugar beet. The last two are currently the main sources of ethanol in Europe [19]. Biodiesel is the fuel that can be produced from straight vegetable oils, edible and non-edible, recycled waste vegetable oils, and animal fat [20–23]. Europe has committed to promotion of the use of biofuels or

other renewable fuels as a substitute for gasoline or diesel in the transport sector [24]. It requires EU member states to set indicative targets for biofuel sales and the reference values are 2% biofuel penetration in gasoline and diesel by 2005, raising it to 5.75% by 2010. There are several factors that need to be taken care before recommending any alternative fuel to be used in existing technologies on a large scale. These factors are stated below.

- Extent of modifications required in the existing hardware, i.e., if any alternative fuel needs extensive modification in the existing hardware involving huge capital then it may be difficult to implement.
- Investment costs for developing infrastructure for processing these alternative fuels. Excessive infrastructure cost may act as a constraint for the development of the energy resource.
- Environmental compatibility compared to conventional fuels. If the new fuel is more polluting then it will be unacceptable as fuel.
- Additional cost to the user in terms of routine maintenance, equipment wear and lubricating oil life. Excessive additional cost will have an adverse effect on the widespread acceptance of this fuel.

A wide variety of fuels can be produced from bio-origin materials and the overview of the conversion routes and fuel produced is given below in Fig. 2.

Ethanol can be produced through fermentation of sugar derived from corn or cellulosic biomass [24]. In 2003, the US consumed nearly 3 billion gallons of ethanol for transportation use. About 90% of this ethanol was produced from corn. Although essentially no ethanol is currently produced from cellulose, research and development is under way to develop and improve the technology required to produce ethanol from cellulosic biomass. Because of the limited supply of corn, ethanol produced from corn cannot meet a large enough fraction of the transportation fuel demand. For example, these 3 billion gallons of ethanol production in the USA already consumes about 11% of total US corn production.

There has been considerable interest in producing fuels from biomass and waste since the oil crises of the last two decades has been reinforced by subsequent environmental concerns and recent political events in the middle-east. Thermo-chemical conversion of wood, straw and refuse includes both

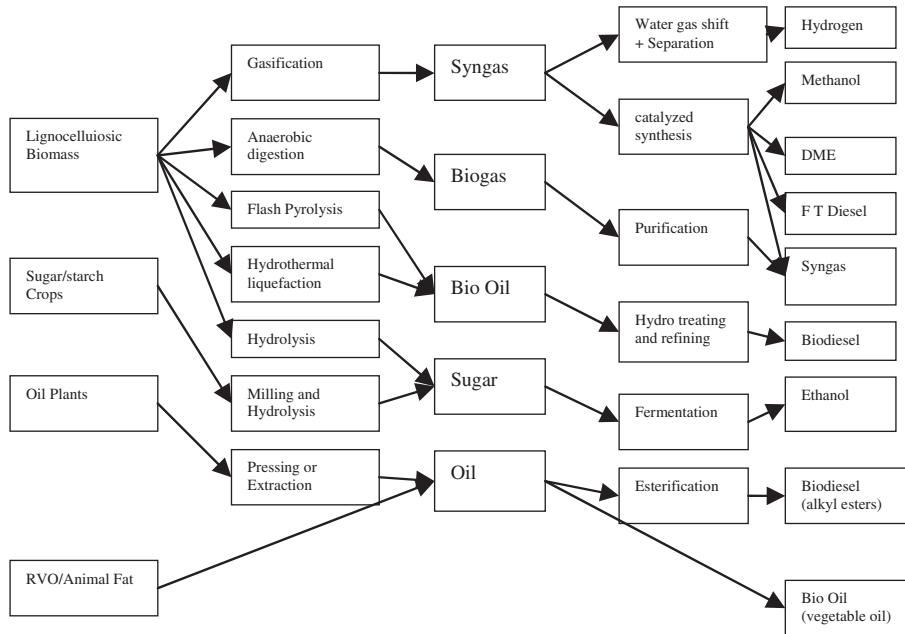


Fig. 2. Overview of conversion routes to biofuels [21].

indirect liquefaction through gasification, and direct liquefaction through pyrolysis and liquefaction in pressurized solvents. Biochemical conversion is based on a different set of feedstock's that includes wood as well as wheat and sugar beet. Both acid and enzyme hydrolysis are included as options, followed by fermentation. The liquid products produced include gasoline and diesel which in some cases require minor refining to convert them into marketable products, and conventional alcohol fuels of methanol and ethanol which established opportunities for utilization. In terms of absolute fuel costs, thermo-chemical conversion offered the lowest cost products, with the least complex processes generally having an advantage. Biochemical routes were the least attractive. The most attractive processes from comparing production costs to product values are generally the alcohol fuels which enjoy a higher market value [21].

1.3. Well to wheel analysis for biofuels

The term "Life Cycle Assessment" is used to assess the total environmental performance of a product all along its lifetime, often referred as from 'cradle to grave'. Other terms, such as life cycle analysis and eco-balance, are also used. When talking about fuels, the proper term in use is "Well-to-Wheel (WTW) Analysis". Similarly in case

of minerals, "Mine-to-Mill Analysis" is carried out. In order to be able to examine the complete fuel-cycle of a transport fuel, the analysis is often divided into following five stages:

- Feedstock production.
- Feedstock transportation.
- Fuel production.
- Fuel distribution.
- Vehicle use.

These stages can be divided even further into a Well-to-Tank (WTT) and Tank-to-Wheel (TTW) portions of the WTW analysis. The WTT analysis considers the fuel from resource recovery to the delivery to the vehicle tank, i.e., the feedstock production, transportation, fuel production and fuel distribution. The TTW analysis considers the fuel economy, i.e., the vehicular use of the fuel. This way, the WTW analysis integrates WTT and TTW into a complete fuel history (Fig. 3).

The data points cluster on trend lines representing the different primary fuel sources, reflecting a constant GHG emission factor (in g CO₂eq/MJ). For the fossil-based fuels, this illustrates the fact that coal, crude oil and natural gas are the primary energy sources for producing the respective fuels. Thus fuels derived from coal give more GHG emissions for the same energy consumption than

equivalent fuels derived from crude oil or natural gas that have lower carbon contents. Equally important though, is the large range of variation along the trend lines—how the fuel is produced and used is just as important as the resource used. The box in the lower left corner of the chart highlights the performance of current gasoline vehicle technology. Many of the possible pathways derived from natural gas, oil or coal produce more GHG emissions and consume more energy than today's conventional fuels pathways. There is more spread when it comes to biomass-based fuels as a range of energy sources are used in this case. Nevertheless the “conventional” biofuels (ethanol, FAME) broadly fall on an intermediate line illustrating the fact that their production still involves a significant amount of fossil energy. The more advanced conversion technologies (e.g. synthetic fuels based on biomass gasification or wind electricity) utilize virtually only renewable energy for the conversion process. As a result GHG emissions are low and the corresponding points lie on an almost horizontal line, very close to the energy axis. For the fossil energy sources, the lines represent the different ways of using that resource. The points along the crude oil line represent different power-train technologies

improving in efficiency from the 2002 gasoline PISI to a 2010 Diesel hybrid. The natural gas line illustrates many ways of using this resource and how different the results can be in terms of energy and GHG emissions. The desirable area of the graph is obviously close to the origin. Taking the crude oil-based fuels as a starting point, it is clear that a majority of the routes towards lower GHG correspond to an increase in primary energy use. Only the combination of the most efficient converters (fuel cells) and the most favorable fuel production pathways result in improved energy efficiency [19].

2. Primary alcohols as fuels for engines

Ethanol has been known as a fuel for many decades. Indeed, when Henry Ford designed the Model T, it was his expectation that ethanol, made from renewable biological materials would be a major automobile fuel. However, gasoline emerged as the dominant transportation fuel in the early twentieth century because of the ease of operation of gasoline engines with the materials then available for engine construction, and a growing supply of cheaper petroleum from oil field discoveries. But

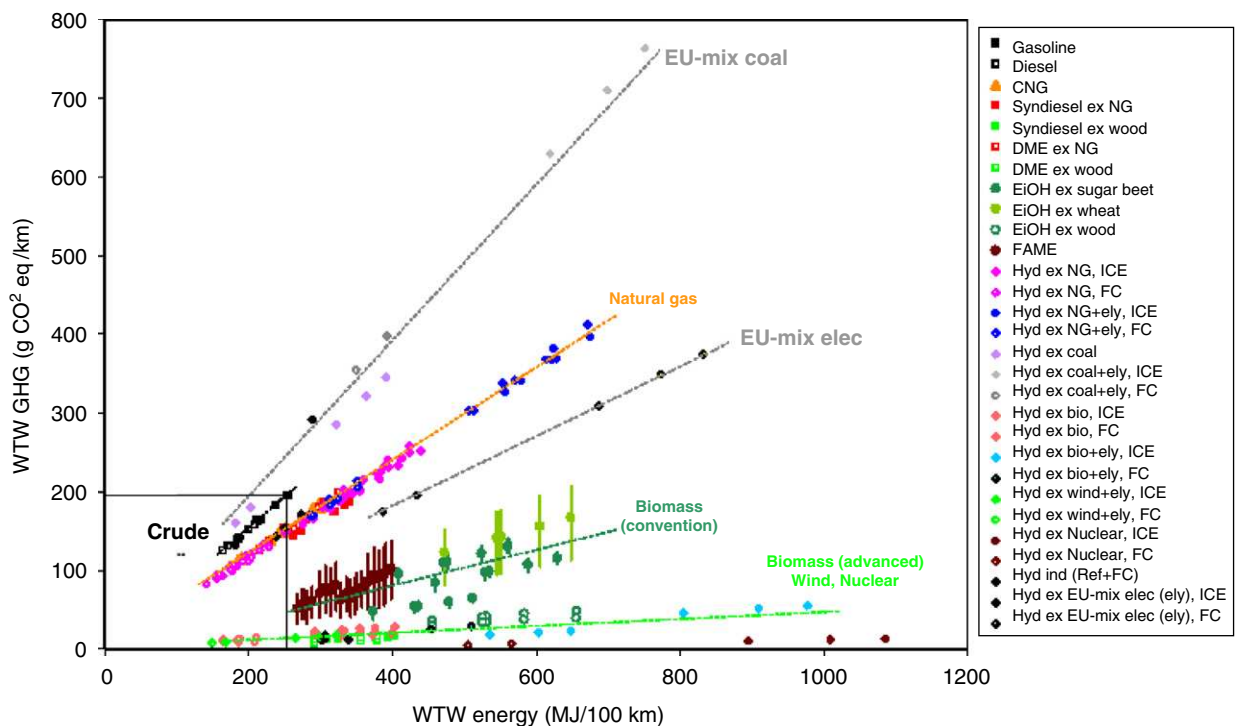


Fig. 3. WTW energy and GHG emissions for all pathways and power-train combinations [19].

gasoline had many disadvantages as an automotive fuel. The “new” fuel had a lower octane rating than ethanol, was much more toxic (particularly when blended with tetra-ethyl lead and other compounds to enhance octane rating), was generally more dangerous, and emitted harmful air pollutants. Gasoline was more likely to explode and burn accidentally, gum would form on storage surfaces, and carbon deposits would form in combustion chamber. Pipelines were needed for distribution from “area found” to “area needed”. Petroleum was much more physically and chemically diverse than ethanol, necessitating complex refining procedures to ensure the manufacture of a consistent “gasoline” product. Because of its lower octane rating relative to ethanol, the use of gasoline meant the use of lower compression engines and larger cooling systems. Diesel engine technology, which developed soon after the emergence of gasoline as the dominant transportation fuel, also resulted in the generation of large quantities of pollutants. However, despite these environmental flaws, fuels made from petroleum have dominated automobile transportation for the past three-quarters of a century. There are two key reasons: first, cost per kilometer of travel has been virtually the sole selection criteria. Second, the large investments made by the oil and auto industries in physical capital, human skills and technology make the entry of a new cost-competitive industry difficult. Until very recently, environmental concerns have been largely ignored.

Ethanol is one of the possible fuels for diesel replacement in compression ignition (CI) engines also. The application of ethanol as a supplementary CI engine fuel may reduce environmental pollution, strengthen agricultural economy, create job opportunities, reduce diesel fuel requirements, and thus contribute in conserving a major commercial energy source. Ethanol was first suggested as an automotive fuel in USA in the 1930s, but was widely used only after 1970. Nowadays, ethanol is used as fuel, mainly in Brazil, and as a gasoline additive for octane number enhancement and improved combustion in USA, Canada and India. As gasoline prices increase and emission regulations become more stringent, ethanol could be given more attention as a renewable fuel or gasoline additive [25,26].

Alcohol is made from renewable resources like biomass from locally grown crops and even waste products such as waste paper, grass and tree

trimmings etc. Alcohol is an alternative transportation fuel since it has properties, which would allow its use in existing engines with minor hardware modifications. Alcohols have higher octane number than gasoline. A fuel with a higher octane number can endure higher compression ratios before engine starts knocking, thus giving engine an ability to deliver more power efficiently and economically. Alcohol burns cleaner than regular gasoline and produce lesser carbon monoxide, HC and oxides of nitrogen [25,27,28]. Alcohol has higher heat of vaporization; therefore, it reduces the peak temperature inside the combustion chamber leading to lower NO_x emissions and increased engine power. However, the aldehyde emissions go up significantly. Aldehydes play an important role in formation of photochemical smog.

Stump et al. [29] examined tailpipe and evaporative emissions from three passenger motor vehicles operating on an ethanol (9% v/v) and a non-oxygenated fuel. A general reduction in hydrocarbon, carbon monoxide, benzene and 1, 3-butadiene emissions was observed when the ethanol fuel was used. Both formaldehyde and acetaldehyde emissions increased (almost double) with the ethanol blend [29].

Methanol (CH_3OH) is a simple compound. It does not contain sulfur or complex organic compounds. The organic emissions (ozone precursors) from methanol combustion will have lower reactivity than gasoline fuels hence lower ozone forming potential. If pure methanol is used then the emission of benzene and PAHs is very low [27]. Methanol gives higher engine efficiency and is less flammable than gasoline but the range of the methanol-fueled vehicle is as much as half less because of lower density and calorific value, so larger fuel tank is required. M100 has invisible flames and it is explosive in enclosed tanks. The cost of methanol is higher than gasoline. Methanol is toxic, and has corrosive characteristics, emits ozone creative formaldehyde. Methanol poses an environmental hazard in case of spill, as it is totally miscible with water. Ethanol is similar to methanol, but it is considerably cleaner, less toxic and less corrosive. It gives greater engine efficiency. Ethanol is grain alcohol, and can be produced from agricultural crops e.g. sugar cane, corn etc. Ethanol is more expensive to produce, has lower range, poses cold starting problems and requires large harvest of these crops. Higher energy input is required in ethanol production compared to other energy crops and it

leads to environmental degradation problems such as soil degradation.

2.1. Properties

Ethanol is isomeric with di-methyl-ether (DME) and both ethanol and DME can be expressed by the chemical formula C_2H_6O . The oxygen atom in ethanol possibly induces three hydrogen bonds. Although, they may have the same physical formula, the thermodynamic behavior of ethanol differs significantly from that of DME on account of the stronger molecular association via hydrogen bonds in ethanol.

The physical properties of alcohols in comparison to CNG, DME and petroleum fuels are given in Table 1.

Alcohol fuels, methanol and ethanol have similar physical properties and emission characteristics as that of petroleum fuels (Table 1). Alcohol's production is cheaper, simple and eco-friendly. This way, alcohol would be a lot cheaper than gasoline fuel. Alcohol can be produced locally, cutting down on fuel transportation costs. Alcohol can be used directly in an engine or it can be blended with gasoline or diesel fuels. Alcohol fuels can be successfully used as IC engine fuels either directly or by preparing biodiesel [33]. Transesterification process utilizes methanol or ethanol and vegetable oils as the process inputs. This route of utilizing alcohol as a diesel engine fuel is definitely a superior route as the toxic emissions (aldehydes) are drastically reduced. The problem of corrosion of various engine parts utilizing alcohol as fuel is also solved by way of transesterification.

Alcohols have been attracting attention worldwide. Consumer wants a cleaner fuel that can lower the risk of harm to environment and health. Governments aim to reduce reliance on imported energy and promote domestic renewable energy programs, which could utilize domestic resources and create new economic activities. Though bio-fuels remain relatively small in use compared to more traditional energy forms, the scenario is changing rapidly. When factors are coupled with vast agri-resources, new technologies that reduce cost, emphasize on environment and pollution abatement and a strong will from both the government and private entrepreneurs; the markets for biofuels are slowly but surely gaining momentum. Fig. 4 shows the world ethanol production in 2001 and projection for 2006.

The fuel "ethanolisation" of the world alcohol industry is set to continue. If all recently announced ethanol projects are implemented, total fuel ethanol production worldwide could grow to 31 billion liters by 2006 against approximately 20 billion liters in 2001.

2.2. Engine modification required and material compatibility

Blends of ethanol in gasoline are commonly used in vehicles designed to operate on gasoline; however, vehicle modification is required for alcohol fueling because its properties are different from those of gasoline (Table 1). Ethanol has low stoichiometric air–fuel ratio and high heat of vaporization that requires carburetor re-calibration and increased heating of the air–fuel mixture to

Table 1
Comparison of various properties of primary alcohols with gasoline and diesel

	Methane	Methanol	Dimethyl ether	Ethanol	Gasoline	Diesel
Formula	CH_4	CH_3OH	CH_3OCH_3	CH_3CH_2OH	C_7H_{16}	$C_{14}H_{30}$
Molecular weight (g/mol)	16.04	32.04	46.07	46.07	100.2	198.4
Density (g/cm ³)	0.00072 ^a	0.792	0.661 ^b	0.785	0.737	0.856
Normal boiling point (°C) [30]	−162	64	−24.9	78	38–204	125–400
LHV (kJ/cm ³) [31]	0.0346 ^a	15.82	18.92	21.09	32.05	35.66
LHV (kJ/g)	47.79	19.99	28.62	26.87	43.47	41.66
Exergy (MJ/l) [30]	0.037	17.8	20.63	23.1	32.84	33.32
Exergy (MJ/kg) [30]	51.76	22.36	30.75	29.4	47.46	46.94
Carbon Content (wt%) [30]	74	37.5	52.2	52.2	85.5	87
Sulfur content (ppm) [32]	~7–25	0	0	0	~200	~250

^aValues per cm³ of vapor at standard temperature and pressure.

^bDensity at $P = 1$ atm and $T = -25$ °C.

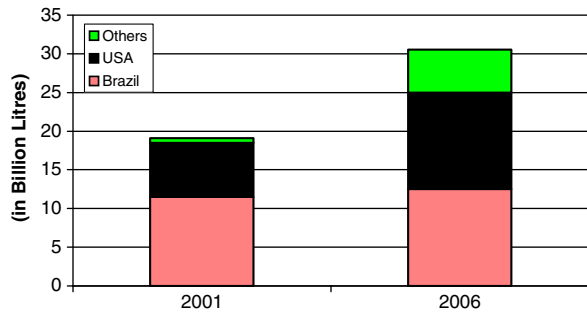


Fig. 4. World ethanol production [34].

provide satisfactory driveability [35]. Brazil has most developed technology for the alcohol fueled Otto cycle (4 stroke) internal combustion engines. In the early 1980s, there were more than 3.5 million alcohol-powered automobiles in Brazil. In order to make alcohol engines more practical, functional, durable, and economical, engineers made several changes in the regular gasoline engines. These included the following:

- Since alcohol does not evaporate as easily as gasoline, the intake manifold had to be redesigned to provide more heating for evaporation.
- The carburetor was regulated in order to change the air/fuel proportions.
- The tin and lead coating of the fuel tank was changed to pure tin.
- The fuel lines (zinc steel alloy) were changed to cadmium brass.
- The fuel-filtering system was changed and re-dimensioned in order to allow a greater fuel flow rates.
- In order to take advantage of the alcohol's much higher octane rating, the compression ratio was increased to about 12:1.
- The valve housings, made of cast-iron, were changed to an iron-cobalt synthetic alloy. This also compensated for the lack of lubrication resulting from the absence of lead in the fuel.
- The catalytic converter's catalyst was changed from palladium and rhodium to palladium and molybdenum, helping further reduce the alcohol engine emissions.

The use of ethanol in gasoline engines in the early 1980s resulted in numerous materials compatibility studies, many of which are also applicable to the effect of ethanol–diesel blends in diesel engines and particularly in the fuel injection system. The quality

of the ethanol has a strong influence on its corrosive effects [36]. In addressing the problems of ethanol corrosion associated with gasoline blends, Brink et al. [37] divided ethanol carburetor corrosion into three categories: general corrosion, dry corrosion and wet corrosion. General corrosion was caused by ionic impurities, mainly chloride ions and acetic acid. Dry corrosion was attributed to the ethanol molecule and its polarity. Wet corrosion is caused by azeotropic water, which oxidizes most metals. Freshly formulated blends containing pH neutral dry ethanol would be expected to have relatively little corrosive effect. However, if a blend has been standing in a tank for sufficient time to allow the ethanol to absorb moisture from the atmosphere, it may tend to be more corrosive as it passes through the fuel injection system [37]. In addition, the fuel may stand in the fuel injection pump for a number of months, for example, in a combine harvester engine, thus allowing the fuel enough time to corrode parts of the pump internally. Corrosion inhibitors have been incorporated in some additive packages used with ethanol–diesel blends. Non-metallic components have also been affected by ethanol with particular reference to elastomeric components such as seals and O-rings in the fuel injection system. These seals tend to swell and stiffen. Resin-bonded or resin-sealed components also are susceptible to swelling and seals may be compromised.

2.3. Engine performance of diesohol and gasohol blends

Ethanol is one of the possible alternative fuels for partial replacement of mineral diesel in CI engines. The application of ethanol as a supplementary fuel may reduce environmental pollution, strengthen agricultural economy, create job opportunities, reduce diesel requirements, and thus contribute in conserving a major commercial energy source [28,38]. Ajav et al. analyzed the effect of using different blends of ethanol–diesel (diesohol) on engine power, brake-specific fuel consumption, brake thermal efficiency, exhaust gas temperatures, and lubricating oil temperature. The results indicate no significant power reduction in the engine operation on ethanol–diesel blends (up to 20%) at a 5% level of significance. Brake-specific fuel consumption increased by up to 9% (with ethanol up to 20%) in the blends as compared to mineral diesel. The exhaust gas temperature, lubricating oil

temperatures and exhaust emissions (CO and NO_x) were lower with operations on ethanol–diesel blends as compared to operation on diesel [38–40].

Ethanol–diesel blends up to 20% can very well be used in present day constant speed CI engines without any modification [41–43]. The brake-specific fuel consumption is slightly increased as shown in Fig. 5, when higher blends of ethanol are used. There is no significant difference in the power produced and the thermal efficiency of the engine as shown in Fig. 6. Exhaust gas temperatures were lower for ethanol–diesel blends than mineral diesel as indicated in Figs. 7 and 8. The engine could be started normally both hot and cold. Up to a 62% reduction in CO emission is possible with the use of ethanol–diesel blends as compared to diesel alone. The NO_x emissions also reduce (up to 24%) when using ethanol–diesel blends [38].

Al-Farayedhi et al. [44] investigated the engine performance using gasohol blends (up to 20%). The results of the oxygenated blends were compared to those of the base fuel and of a leaded fuel prepared

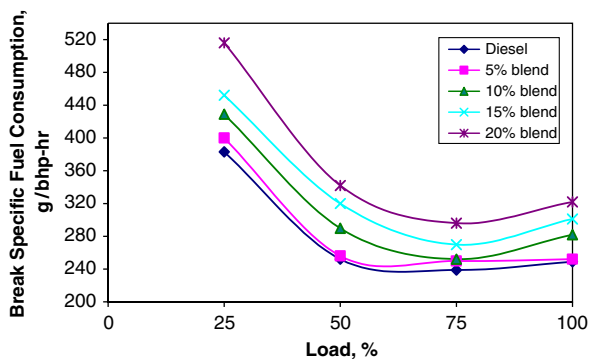


Fig. 5. Brake specific fuel consumption for different diesohol blends [38].

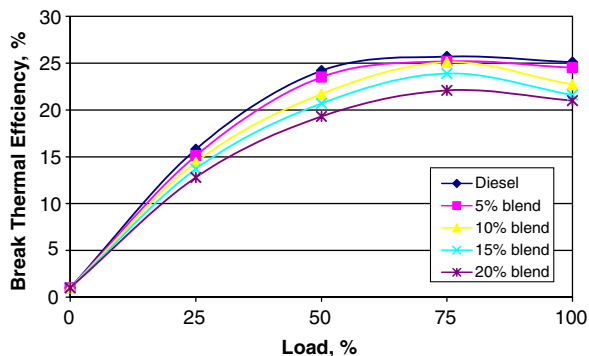


Fig. 6. Brake thermal efficiency for different diesohol blends [38].

by adding tetra ethyl lead (TEL) to the base fuel. The engine's maximum output and thermal efficiency were evaluated at a variety of operating conditions.

The maximum brake torque and bmeip results versus engine speed for all the tested fuels are shown in Figs. 9 and 10. Consistent and persisting fluctuations in the maximum torque measurements were observed. These fluctuations were closely examined and eventually linked to abnormal vibrations in the test setup. The confidence of torque measurement is found to be 95%. The base fuel produced the lowest brake torque among all the tested fuels. The leaded fuel exhibited a substantial increase in the brake torque with respect to the base fuel. This substantial increase is a result of the improved anti-knock behavior due to the addition of TEL, which raised the octane number from 84.7 for the base fuel to 92 for the leaded fuel. The improved anti-knock behavior allowed a more

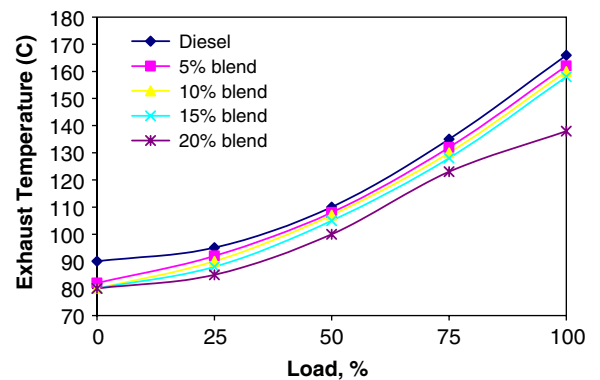


Fig. 7. Exhaust gas temperature for different diesohol blends [38].

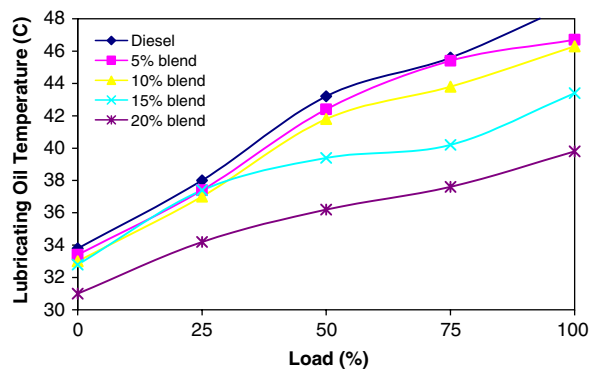


Fig. 8. Lubricating oil temperature for different diesohol blends [38].

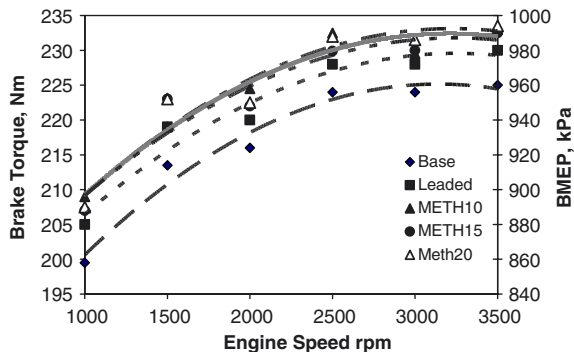


Fig. 9. Brake torque and mean effective pressure at wide-open throttle for the methanol blends [44].

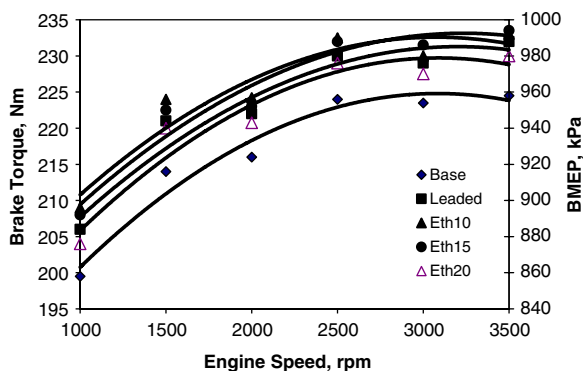


Fig. 10. Brake torque and mean effective pressure at wide-open throttle for the ethanol blends [44].

advanced MBT timing that results in higher combustion pressure and thus higher exerted torque and bmeP. The results for the methanol blends Fig. 9 indicate an increasingly improving brake torque with the increasing methanol ratio in the blend. The improvement in the brake torque persists over the whole range of the tested engine speed. This gain in brake torque obtained with methanol blends can be attributed to better anti-knock behavior of these blends and the improvement in engine volumetric efficiency.

The results for the ethanol blends (Fig. 10) show a significant improvement in brake torque with the 10% v/v ethanol blend (ETH10) when compared to the base fuel. At low engine speeds, further increase of ethanol ratio had no effect on the brake torque. At high speeds, the 15% v/v ethanol blend (ETH15) performed slightly better but further addition of ethanol resulted in a decline in the brake torque. Similar to the methanol blends, the gain in brake torque can be attributed to the improvement in antiknock behavior and volumetric efficiency [43].

Figs. 11 and 12 show the variation of exhaust gas temperature corresponding to all tested fuels. In general, the highest exhaust temperature is observed with the base fuel, and the lowest with the leaded fuel. In addition, the exhaust temperature decreases as the oxygenate ratio in the blend increases. These variations in exhaust temperatures can be attributed to the increase in thermal efficiency and/or the decrease in the combustion temperatures. The increase in thermal efficiency means that a larger portion of combustion heat has been converted into work and therefore lower exhaust temperatures can be expected. In addition, the lower combustion temperatures characterizing the oxygenated blends are expected to result in lower exhaust temperatures [44].

2.4. Regulated and unregulated emissions from ethanol operated engines

Combustion engine emissions have been shown to be major contributor to air pollution in urban areas. Vehicle emissions are divided into two groups; regulated and unregulated pollutants. Regulated pollutants are carbon monoxide (CO), nitrogen oxides (NO_x), and unburned fuel or partly oxidized HC. The levels of emissions of these pollutants are specified by legislations. Unregulated pollutants include polycyclic aromatic hydrocarbons (PAHs), methane, aldehydes, carbon dioxide, other trace organic emissions and carbon deposits. Carbon deposits increase engine wear, while some of the PAH isomers are known to be carcinogenic and mutagenic. The main effect of 10% ethanol additions to gasoline on pollutant formation is that PM and CO emissions get significantly reduced. For some of the vehicles tested, CO_2 emissions were also significantly reduced and overall it led to a small deterioration in fuel economy (although this was not significant at 95% confidence level). NO_x emissions were not significantly influenced, however, for some of the vehicles tested, acetaldehyde emissions significantly increased.

The observed effects of ethanol addition were consistent with the anticipated effects on combustion chemistry and the response of different vehicle technologies to these. In particular, the vehicles that showed the greatest enhancement of fuel economy were those with modern engine management systems incorporating knock sensors which would confer the ability to optimize timing in response to an octane number increase [27,45–48].

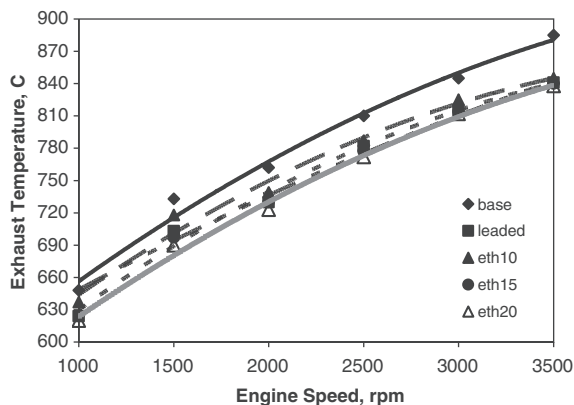


Fig. 11. Exhaust temperature at wide-open throttle for the ethanol blends [44].

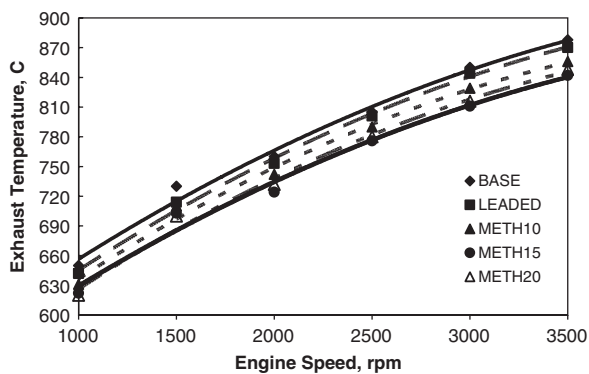


Fig. 12. Exhaust temperature at wide-open throttle for the methanol blends [44].

2.4.1. Carbon dioxide

CO₂ is released into the atmosphere when ethanol (like other fuels) is burned in an engine. However, this CO₂ is recycled into organic tissues during plant growth. Only about 40% or less of the organic matter is actually removed from farm fields for ethanol production. The rest is returned to the soil as organic matter, increasing fertility and reducing soil erosion. With modern conservation farming practices, this soil organic-matter will build up, representing a net removal of CO₂ from the atmosphere. An increase of only 1% in the soil organic matter level means an atmospheric reduction of over 40 ton of CO₂ per hectare of farmland. Ethanol use in gasoline has tremendous potential for a net reduction in atmospheric CO₂ levels.

A study to calculate the life-cycle emissions from various alternative fuels for heavy-duty vehicles also predict the great environmental benefit attained from using ethanol as vehicular fuel. Biodiesel and

ethanol are climate friendly, even when considered on a life-cycle basis [49–53]. They have the lowest lifecycle greenhouse gas emissions (in grams GHG per kilometer traveled). In fact, both emit larger quantities of CO₂ than conventional fuels, but as most of this is from renewable carbon stocks, that fraction is not counted towards the GHG emissions from the fuel.

Table 2 shows fuel-cycle fossil fuel GHG emission (in CO₂ equivalent) from difference conventional and alternative fuels.

2.4.2. Carbon monoxide

CO, formed by the incomplete combustion of fuels, is produced most readily from petroleum fuels, which contain no oxygen in their molecular structure. Since ethanol and other “oxygenated” compounds contain oxygen, their combustion in automobile engines is more complete. The result is a substantial reduction in CO emissions. Research shows that reductions range up to 30%, depending on type and age of engine/vehicle, the emission control system used, and the atmospheric conditions in which the vehicle operates. Because of health concerns over CO, the 1990 amendment to the US Clean Air Act mandated the use of oxygenated gasoline in major urban centers during winter (when atmospheric CO levels are highest) to reduce this pollution [47,54].

2.4.3. Hydrocarbons

Because of its high octane rating, adding ethanol to gasoline leads to reduction or removal of aromatic HC's (such as benzene), and other hazardous high-octane additives commonly used to replace TEL lead in gasoline [28].

2.4.4. Ozone

Because of its effect in reducing HC and CO in exhaust, adding ethanol to gasoline results in an overall reduction in exhaust ozone-forming potential [18]. Ethanol has no significant effect on emissions of nitrous oxide, another common contributor to atmospheric ozone. Adding ethanol to gasoline can potentially increase the volatility of gasoline. This potential is controlled if all ethanol-blended gasoline sold meets the volatility standards required for other types of gasoline. The US Clean Air Act allows gasohol (gasoline plus 10% ethanol) to have a higher volatility than that of gasoline. This results in greater “volatile organic compounds” emissions.

Table 2
Fuel-cycle fossil fuel greenhouse gas emissions (g/MJ) for heavy-duty vehicles in CO₂-equivalents [49]

	Diesel	LSD	ULS	LPG	CNG	LNG	E95 (wood)	BD20	BD100
Pre-combustion	11	12	13	11	6	9	−29	2	−41
Combustion	69	69	69	59	54	55	65	84	89
Total	80	81	82	70	60	64	36	87	48

Adding ethanol to gasoline does emit slightly greater amount of aldehydes during combustion. Yet the resulting concentrations are extremely small and are effectively reduced by the three-way catalytic converter in the exhaust systems of all modern contemporary vehicles.

The addition of ethanol to the fuel up to 10% w/w result in an increase in the Reid vapor pressure, indicating increased evaporative emissions for ethanol blends. Generally, benzene and toluene emissions decrease by ethanol addition to gasoline although this beneficial effect of ethanol was eliminated after the operation of the catalyst. Acetic acid was detected in exhaust gases in some cases only for the base and the 3% ethanol blend fuel [46,55–57].

2.4.5. Oxides of nitrogen

A clear trend of reduced HC and CO emissions and increased NO_x emissions were observed as the ethanol concentration in the fuel increased from 0% to 20% (Fig. 13). The standard vehicle was noted to operate at air/fuel ratios significantly richer than stoichiometric, with an average air/fuel ratio running on gasoline of approximately 12.2:1 over the FTP cycle. This equates to an equivalence ratio, when operated on gasoline only fuel, of approximately 1.2. For leaner base conditions, the trend could be the opposite, with HC emissions increasing and NO_x emissions reducing as the ethanol content of the fuel is increased [58].

2.4.6. Unregulated emissions

With increase of ethanol content in the fuel blend, acetaldehyde emissions increase. Since acetaldehyde is an intermediate product from the partially oxidized quenched fuel, it is possible that more acetaldehyde emissions are formed from ethanol fueling under some operating conditions. It is also observed that acetaldehyde emissions have close relationship with the engine load and ethanol content in the blend. With increase in load from

idling, acetaldehyde emissions gradually decrease to their minima at medium loads, then increase again at high engine loads. High acetaldehyde emissions are attributed to thick quenching layer formed by a large amount of ethanol in the fuel at high loads and also due to low oxidation rate of acetaldehyde at low engine loads due to low combustion temperatures and exhaust gas temperatures. There are other toxic emissions (unregulated), which should be considered to ascertain the impact of ethanol-blended fuels such as acetaldehyde, formaldehyde, propionaldehyde and acrolein, benzene, ethylbenzene, 1-3 butadiene, acrolein, hexane, toluene, xylene, and fine particulate. Benzene emissions were reduced up to 50% with the ethanol-blended fuels. Emissions of 1,3-butadienes were also substantially decreased, with reduction ranging from 24% to 82%. Isolated trends were noted for certain PAHs. There was a decrease in 1-nitrobenzene with use of ethanol in all case. There was also a general increase in the proportion of heavy PAHs in the particulate phase with ethanol use, and although less pronounced, general decreases in light PAHs in the particulate phase [59].

3. Vegetable oils as engine fuels

Dr. Rudolf Diesel invented the diesel engine to run on a host of fuels including coal dust suspended in water, heavy mineral oil, and, vegetable oils. Dr. Diesel's first engine experiments were catastrophic failures, but by the time he showed his engine at the World Exhibition in Paris in 1900, his engine was running on 100% peanut oil. Dr. Diesel (Fig. 14) was visionary. In 1911 he stated "The diesel engine can be fed with vegetable oils and would help considerably in the development of agriculture of the countries, which use it". 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 time". Since

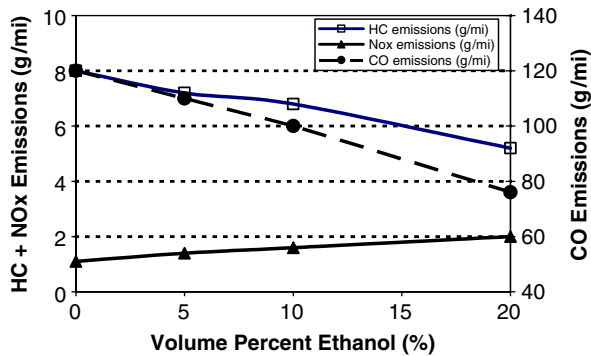


Fig. 13. Alcohol fueled vehicle emission on FTP driving cycle [58].

Dr. Diesel's untimely death in 1913, his engine has been modified to run on the polluting petroleum fuel, now known as "diesel". Nevertheless, his ideas on agriculture and his invention provided the foundation for a society fueled with clean, renewable, locally grown fuel [60].

In the 1930s and 1940s, vegetable oils were used as diesel substitutes from time to time, but usually only in emergency situations. Recently, because of increase in crude oil prices, limited resources of fossil oil and environmental concerns, there has been a renewed focus on vegetable oils and animal fats to make biodiesel. Continued and increasing use of petroleum will intensify local air pollution and magnify the global warming problems caused by carbon dioxide. In a particular case, such as the emission of pollutants in the closed environment of underground mines, biodiesel has the potential to reduce the level of pollutants and the level of potential for probable carcinogens [61].

The advantages of using vegetable oils as fuels are:

- Vegetable oils are liquid fuels from renewable sources.
- They do not over-burden the environment with emissions.
- Vegetable oils have potential for making marginal land productive by their property of nitrogen fixation in the soil.
- Vegetable oil's production requires lesser energy input in production.
- Vegetable oils have higher energy content than other energy crops like alcohol. Vegetable oils have 90% of the heat content of diesel and they have a favorable output/input ratio of about 2–4:1 for un-irrigated crop production.

- The current prices of vegetable oils in world are nearly competitive with petroleum fuel price.
- Vegetable oil combustion has cleaner emission spectra.
- Simpler processing technology.

But

- these are not economically feasible yet and
- need further R&D work for development of on-farm processing technology.

Due to the rapid decline in crude oil reserves, the use of vegetable oils as diesel fuels is again promoted in many countries. Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soybean oil in the USA, rapeseed and sunflower oils in Europe, palm oil in Southeast Asia (mainly Malaysia and Indonesia), and coconut oil in Philippines are being considered as substitutes for mineral diesel.

An acceptable alternative fuel for engine has to fulfill the environmental and energy security needs without sacrificing operating performance. Vegetable oils can be successfully used in CI engine through engine modifications and fuel modifications. Engine modifications include dual fueling, injection system modification, heated fuel lines etc. Fuel modifications include blending of vegetable oils with diesel, transesterification, cracking/pyrolysis, micro-emulsion, and hydrogenation to reduce polymerization and viscosity [63].

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, 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 oil in its raw form cannot be used in engines. It has to be converted to a more engine-friendly fuel called biodiesel. System design approach has taken care to see that these modified fuels can be utilized in the existing diesel engine without substantial hardware modification. 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 any country.

In its simplest form, the carbon cycle of vegetable oil consists 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 CO_2 through processes of combustion. It is appropriate to mention here that the CO_2 released by petroleum diesel was fixed from the atmosphere during the formative years of the earth, whereas the CO_2 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 CO_2 and its release after combustion of biodiesel is quite small as compared (few years) to the cycle time of petroleum based fuels (Fig. 15) (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 substantially lower quantities of most of the regulated pollutants compared to mineral diesel [63]. Biodiesel has comparable energy density, cetane number, heat of vaporization, and stoichiometric air/fuel ratio with mineral diesel. The large molecular size of the component triglycerides result in the oil having higher viscosity compared with that of mineral diesel. Viscosity affects the handling of the fuels by pump and injector system, and the shape of fuel spray. The high jet penetration and poor atomization results in larger droplets. The fuel Jet tends to be a solid stream instead of spray of small droplets hence the fuel does not get mixed with air required for burning. Larger droplets have poor combustion leading to loss of engine power and fuel economy. In small engines, the fuel spray may even impinge upon the cylinder walls, washing away the lubricating oil film and causing the dilution of crank case oil leading to excessive wear of moving parts.

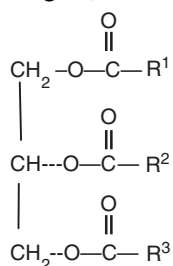
3.1. Vegetable oil chemistry

The petroleum diesel fuel molecules are saturated non-branched molecules with carbon atoms ranging between 12 and 18, whereas vegetable oils are the mixture of organic compounds ranging from simple straight chain compound to complex structure of proteins and fat-soluble vitamins. Fats and oils are primarily water-insoluble, hydrophobic substances in the plant and animal kingdom that are made up of one mole of glycerol and three moles of fatty acids and are commonly referred to as triglycerides.



Fig. 14. Dr. Rudolf Diesel.

Vegetable oils are usually triglycerides generally with a number of branched chains of different lengths, and have structure notation as shown,



where R^1 , R^2 , R^3 represent hydrocarbon chain of fatty acids.

Fatty acids vary in carbon chain length and in the number of unsaturated bonds (double bonds). The structures of common fatty acids are given in Table 3, and fatty acid compositions of some vegetable oils are given in Table 4.

Vegetable oils have about 10% less heating value than diesel due to the oxygen content in the molecule and the viscosity of vegetable oil is several times higher than that of mineral diesel due to large molecular weight and complex chemical structure. The fuel related properties (Physical and Thermal) of some of the vegetable oils are listed in Table 5.

The high viscosity of vegetable oil, 35–60 cSt compared to 4 cSt for diesel at 40 °C, leads to problem in pumping and spray characteristics (atomization and penetration etc.). The inefficient mixing of oil with air contributes to incomplete combustion. High flash point attributes to its lower volatility characteristics. This results in high carbon deposit formation, injector coking, piston ring sticking and lubrication oil dilution and oil degradation. The combination of high viscosity and low volatility of vegetable oils cause poor cold starting, misfire and ignition delay. Some of the short- and long-term problems associated with utilization of vegetable oils in engine are shown in Table 6. This

table also discusses probable reasons and potential solutions for these problems. Polyunsaturated nature of the vegetable oils cause long-term problems such as gum formation, ring sticking etc. Because of these problems, vegetable oils must be chemically modified to a more suitable and compatible fuel for existing engines.

3.2. Vegetable oil utilization as engine fuel

Neat vegetable oils are not suitable as fuel for diesel engines; hence they have to be modified to

Table 3
Chemical structure of common fatty acids [64]

Fatty acid	Systematic name	Structure ^a	Formula
Lauric	Dodecanoic	12:0	C ₁₂ H ₂₄ O ₂
Myristic	Tetradecanoic	14:0	C ₁₄ H ₂₈ O ₂
Palmitic	Hexadecanoic	16:0	C ₁₆ H ₃₂ O ₂
Stearic	Octadecanoic	18:0	C ₁₈ H ₃₆ O ₂
Arachidic	Eicosanoic	20:0	C ₂₀ H ₄₀ O ₂
Behenic	Docosanoic	22:0	C ₂₂ H ₄₄ O ₂
Lignoceric	Tetracosanoic	24:0	C ₂₄ H ₄₈ O ₂
Oleic	cis-9-Octadecenoic	18:1	C ₁₈ H ₃₄ O ₂
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	C ₁₈ H ₃₂ O ₂
Linolenic	cis-9,cis-12, cis-15-Octadecatrienoic	18:3	C ₁₈ H ₃₀ O ₂
Erucic	cis-13-Docosenoic	22:1	C ₂₂ H ₄₂ O ₂

^axx:y indicates xx carbons in the fatty acid chain with y double bonds.

Table 4
Chemical composition of vegetable oils [64]

Vegetable oil	Fatty acid composition (wt%)									
	14:0	16:0	18:0	20:0	22:0	24:0	18:1	22:1	18:2	18:3
Corn	0	12	2	Tr	0	0	25	0	6	Tr
Cottonseed	0	28	1	0	0	0	13	0	58	0
Crambe	0	2	1	2	1	1	19	59	9	7
Linseed	0	5	2	0	0	0	20	0	18	55
Peanut	0	11	2	1	2	1	48	0	32	1
Rapeseed	0	3	1	0	0	0	64	0	22	8
Safflower	0	9	2	0	0	0	12	0	78	0
H.O. Safflower	Tr	5	2	Tr	0	0	79	0	13	0
Sesame	0	13	4	0	0	0	53	0	30	0
Soya bean	0	12	3	0	0	0	23	0	55	6
Sunflower	0	6	3	0	0	0	17	0	74	0
Rice-bran	0.4–0.6	11.7–16.5	1.7–2.5	0.4–0.6	—	0.4–0.9	39.2–43.7	—	26.4–35.1	—
Sal	—	4.5–8.6	34.2–44.8	6.3–12.2	—	—	34.2–44.8	—	2.7	—
Mahua	—	16.0–28.2	20.0–25.1	0.0–3.3	—	—	41.0–51.0	—	8.9–13.7	—
Neem	0.2–0.26	13.6–16.2	14.4–24.1	0.8–3.4	—	—	49.1–61.9	—	2.3–15.8	—
Karanja	—	3.7–7.9	2.4–8.9	—	—	1.1–3.5	44.5–71.3	—	10.8–18.3	—

Tr: Traces.

bring their combustion-related properties closer to those of mineral diesel. This fuel modification is mainly aimed at reducing the viscosity to get rid of flow and combustion-related problems. Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of HC-based fuels. Vegetable oils can be used through at least four ways:

- Direct use and blending.
- Micro-emulsion.
- Pyrolysis (thermal cracking).
- Transesterification.

3.2.1. Direct use and blending

Caterpillar (Brazil) in 1980 used pre-combustion chamber engines with a mixture of 10% vegetable oil to maintain total power without any alterations or adjustments to the engine. At that point, it was not practical to substitute 100% vegetable oil for diesel fuel, but a blend of 20% vegetable oil and 80% mineral diesel was successful. Some short-term experiments used up to a 50/50 ratio [66]. Pramanik et al. [67] found that 50% blend of Jatropha oil can be used in diesel engine without any major operational difficulties but further study is required for the long-term durability of the engine. Direct use of vegetable oils and/or the use of blends of the oils have generally been considered to be not satisfac-

Table 5
Physical and thermal properties of vegetable oils [64]

Vegetable oil	Kinematic viscosity ^a	Cetane no.	Heating value (MJ/kg)	Cloud point (°C)	Pour point (°C)	Flash point (°C)	Density (Kg/l)	Carbon residue (wt%)	Ash (wt%)	Sulfur (wt%)
Corn	34.9	37.60	39.50	−1.1	−40.0	277	0.9095	0.24	0.010	0.01
Cotton-seed	33.5	41.8	39.5	1.7	−15.0	234	0.9148	0.24	0.010	0.01
Cramble	53.6	44.6	40.5	10.0	−12.2	274	0.9044	0.23	0.050	0.01
Linseed	22.2	34.6	39.3	1.7	−15.0	241	0.9236	0.22	<0.01	0.01
Peanut	39.6	41.8	49.8	12.8	−6.7	271	0.9026	0.24	0.005	0.01
Rapeseed	37.0	37.6	39.7	−3.9	−31.7	246	0.9115	0.30	0.054	0.01
Safflower	31.3	41.3	39.5	18.3	−6.7	260	0.9144	0.25	0.006	0.01
H.O. safflower	41.2	49.1	39.5	−12.2	−20.6	293	0.9021	0.24	<0.001	0.02
Sesame	35.5	40.2	39.3	−3.9	−9.4	260	0.9133	0.25	<0.01	0.01
Soyabean	32.6	37.9	39.6	−3.9	−12.2	254	0.9138	0.27	<0.01	0.01
Sunflower	33.9	37.1	39.6	7.2	−15.0	274	0.9161	0.23	<0.01	0.01
Palm	39.6	42.0	—	31.0	—	267	0.9180	—	—	—
Babassu	30.3	38.0	—	20.0	—	150	0.9460	—	—	—
Tallow	—	—	40.0	—	—	201	—	6.21	—	—

^aAt 40 °C.

Table 6
Problems and potential solutions for using vegetable oils as engine fuels [65,66]

Problem	Probable cause	Potential solution
<i>Short-term</i>		
1. Cold weather starting	High viscosity, low cetane, and low flash point of vegetable oils	Preheat fuel prior to injection. Chemically alter fuel to an ester
2. Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in vegetable oil. Ash.	Partially refine the oil to remove gums. Filter to 4 microns
3. Engine knocking	Very low cetane of some oils. Improper injection timing.	Adjust injection timing. Preheat fuel prior to injection. Chemically alter fuel to an ester
<i>Long-term</i>		
4. Coking of injectors and carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load.	Heat fuel prior to injection. Switch engine to diesel when operating at part load. Chemically alter the vegetable oil to an ester.
5. Excessive engine wear	High viscosity, incomplete combustion of fuel. Poor combustion at part load. Possibly free fatty acids in vegetable oil. Dilution of engine lubricating oil due to blow-by of vegetable oil.	Heat fuel prior to injection. Switch engine to diesel when operating at part load. Chemically alter the vegetable oil to an ester. Increase lubricating oil changes. Lubricating oil additives to inhibit oxidation.
6. Failure of engine lubricating oil due to polymerization	Collection of poly-unsaturated vegetable oil blow-by in crank-case to the point where polymerization occurs	Same as in 5.

tory and impractical for both direct and indirect diesel engines. The high viscosity, acid composition, free fatty acid content, as well as gum formation due

to oxidation, polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems. The probable

reasons for the problems and the potential solutions are shown in Table 6 [65,66].

3.2.2. Micro-emulsions

To solve the problem of the high viscosity of vegetable oils, micro-emulsions with solvents such as methanol, ethanol and 1-butanol have been investigated. A micro-emulsion is defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimension generally in the 1–150 nm range, formed spontaneously from two normally immiscible liquids. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. Short-term performance of micro-emulsions of aqueous ethanol in soybean oil was nearly as good as that of no. 2 diesel, in spite of the lower cetane number and energy content [64].

3.2.3. Pyrolysis (thermal cracking)

Pyrolysis is the conversion of one substance into another by means of heat or by heat in presence of a catalyst. The paralyzed material can be vegetable oils, animal fats, natural fatty acids or methyl esters of fatty acids. The pyrolysis of fats has been investigated for more than 100 years, especially in those areas of the world that lack deposits of petroleum. Many investigators have studied the pyrolysis of triglycerides to obtain products suitable for diesel engine. Thermal decomposition of triglycerides produces alkanes, alkenes, alkanes, alkanes, aromatics and carboxylic acids [66,67].

3.2.4. Transesterification

In organic chemistry, transesterification is the process of exchanging the alkoxy group of an ester compound by another alcohol. The reactions are often catalyzed by an acid or a base. Transesterification is crucial for producing biodiesel from biolipids. The transesterification process is the reaction of a triglyceride (fat/oil) with a bio-alcohol to form esters and glycerol [68–71]. The details of the process of transesterification and biodiesel production are given in following paragraphs.

4. Biodiesel as engine fuel

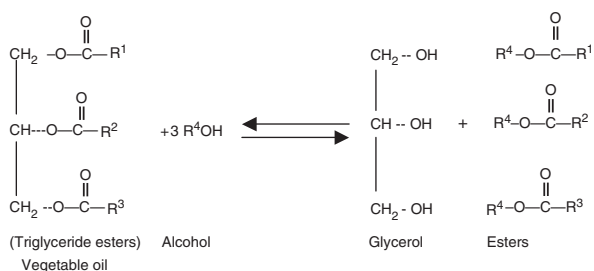
The best way to use vegetable oil as fuel is to convert it in to biodiesel. Biodiesel is the name of a clean burning mono-alkyl ester-based oxygenated fuel made from natural, renewable sources such as new/used vegetable oils and animal fats. The

resulting biodiesel is quite similar to conventional diesel in its main characteristics. Biodiesel contains no petroleum products, but it is compatible with conventional diesel and can be blended in any proportion with mineral diesel to create a stable biodiesel blend. The level of blending with petroleum diesel is referred as Bxx, where xx indicates the amount of biodiesel in the blend (i.e. B10 blend is 10% biodiesel and 90% diesel. It can be used in CI engine with no major modification in the engine hardware.

4.1. Transesterification

Vegetable oils have to undergo the process of transesterification to be usable in internal combustion engines. Biodiesel is the product of the process of transesterification. Biodiesel is biodegradable, non-toxic and essentially free from sulfur; it is renewable and can be produced from agriculture and plant resources. Biodiesel is an alternative fuel, which has a correlation with sustainable development, energy conservation, management, efficiency and environmental preservation.

Transesterification is the reaction of a fat or oil with an alcohol to form esters and glycerol. Alcohol combines with the triglycerides to form glycerol and esters. A catalyst is usually used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is required to shift the equilibrium to the product side. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol and amyl alcohol [66]. Alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification and is most often used commercially [66–71].



R^1, R^2, R^3, R^4 represent various alkyl group.

The process of transesterification brings about drastic change in viscosity of vegetable oil. The biodiesel thus produced by this process is totally

miscible with mineral diesel in any proportion. Biodiesel viscosity comes very close to that of mineral diesel hence no problems in the existing fuel handling system. Flash point of the biodiesel gets lowered after esterification and the cetane number gets improved. Even lower concentrations of biodiesel act as cetane number improver for biodiesel blend. Calorific value of biodiesel is also found to be very close to mineral diesel. Some typical observations from the engine tests suggested that the thermal efficiency of the engine generally improves, cooling losses and exhaust gas temperature increase, smoke opacity generally gets lower for biodiesel blends. Possible reason may be additional lubricity properties of the biodiesel; hence reduced frictional losses (FHP). The energy thus saved increases thermal efficiency, cooling losses and exhaust losses from the engine. The thermal efficiency starts reducing after a certain concentration of biodiesel. Flash point, density, pour point, cetane number, calorific value of biodiesel comes in very close range to that of mineral diesel [70–71].

Diesel engine can perform satisfactory for long run on biodiesel without any hardware modifications. Twenty percent biodiesel is the optimum concentration for biodiesel blend with improved performance. Increase in exhaust temperature however lead to increased NO_x emissions from the engine. While short-term tests are almost positive, long-term use of neat vegetable oils or their blend with diesel leads to various engine problems such as, injector coking, ring sticking, injector deposits etc. [72,73]. High viscosity, low volatility and a tendency for polymerization in the cylinder are root causes of many problems associated with direct use of these oils as fuels. The process of transesterification yield vegetable oil ester, which has shown promises as alternative diesel fuel as a result of improved viscosity and volatility. Several researchers investigate the different vegetable oil esters and find esters comparable to mineral diesel [69–74]. The yield of biodiesel in the process of transesterification is affected by several process parameters/variables.

The most important variables affecting the yield of biodiesel from transesterification are:

- Reaction temperature.
- Molar ratio of alcohol and oil.
- Catalyst.
- Reaction time.
- Presence of moisture and free fatty acids (FFA).

4.1.1. The effect of reaction temperature

The rate of reaction is strongly influenced by the reaction temperature. However, given enough time, the reaction will proceed to near completion even at room temperature. Generally, the reaction is conducted close to the boiling point of methanol (60–70 °C) at atmospheric pressure. The maximum yield of esters occur at temperatures ranging from 60 to 80 °C at a molar ratio (alcohol to oil) of 6:1 [64,66–71]. Several researchers have studied the effect of temperature on conversion of oils and fats into biodiesel. Freedman et al. [69] studied the transesterification of refined soybean oil with methanol (6:1), 1% NaOH catalyst, at three different temperatures 60, 45 and 32 °C. After 0.1 h, ester yields were 94%, 87% and 64% for 60, 45 and 32 °C, respectively. After 1 h, ester formation was identical for 60 and 45 °C reaction temperature runs and only slightly lower for 32 °C. It shows that temperature clearly influenced the reaction rate and yield of esters and transesterification can proceed satisfactorily at ambient temperatures, if given enough time, in the case of alkaline catalyst.

4.1.2. The effect of molar ratio

Another important variable affecting the yield of ester is the molar ratio of alcohol to vegetable oil. The stoichiometry of the transesterification reaction requires 3 mole of alcohol per mole of triglyceride to yield 3 mole of fatty esters and 1 mole of glycerol. To shift the transesterification reaction to the right, it is necessary to use either a large excess of alcohol or remove one of the products from the reaction mixture continuously. The second option is preferred wherever feasible, since in this way, the reaction can be driven towards completion. When 100% excess methanol is used, the reaction rate is at its highest. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight. Freedman et al. [69] studied the effect of molar ratio (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cottonseed oils behaved similarly and achieved highest conversions (93–98%) at a 6:1 molar ratio. Ratios greater than 6:1 do not increase yield (already 98–99%), however, these interfere with separation of glycerol.

4.1.3. The effect of catalyst

Catalysts are classified as alkali, acid, or enzymes. Alkali-catalyzed transesterification is much faster than acid-catalyzed reaction. However, if a vegetable

oil has high free fatty acid and water content, acid-catalyzed transesterification reaction is suitable. Partly due to faster esterification and partly because alkaline catalysts are less corrosive to industrial equipment than acidic catalysts, most commercial transesterification reactions are conducted with alkaline catalysts. Sodium methoxide was found to be more effective than sodium hydroxide. Sodium alkoxides are among the most efficient catalysts used for this purpose, although NaOH, due to its low cost, has attracted its wide use in large-scale transesterification. The alkaline catalyst concentrations in the range of 0.5–1% by weight yield 94–99% conversion of vegetable oils into esters. Further increase in catalyst concentration does not increase the conversion and it adds to extra costs because it is necessary to remove the catalyst from the reaction products at the end [64,69,70]. Methanol can quickly react with triglycerides and NaOH is easily dissolved in it. The reaction can be catalyzed by alkalis, acids, or enzymes. The alkalis include NaOH, KOH, carbonates and corresponding sodium and potassium alkoxides such as sodium methoxide, sodium ethoxide, sodium propoxide and sodium butoxide. Sulfuric acid, sulfonic acids and hydrochloric acid are usually used as acid catalysts. Lipases also can be used as biocatalysts.

4.1.4. The effect of reaction time

The conversion rate increases with reaction time. Freedman et al. [69] transesterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60 °C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93–98%). Ma and Hanna [66] studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef tallow. From 1 to 5 min, the reaction proceeded very fast. The apparent yield of beef tallow methyl esters surged from 1% to 38%.

4.1.5. The effect of moisture and FFA

For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the

separation of ester and glycerol and water washing difficult. The glycerol is then removed by gravity separation and remaining ester is mixed with hot water for separation of catalyst. Moisture can be removed using silica gel. Ester formation eliminates almost all the problems associated with vegetable oils. Saponification reaction also takes place simultaneously along with transesterification process but soap formation is not a major problem if presence of water is less than 1% [66–71].

Starting materials used for alkali-catalyzed transesterification of triglycerides must meet certain specifications. The glyceride should have an acid value less than 1 and all reactants should be substantially anhydrous. If the acid value was greater than 1, more NaOH is required to neutralize the FFA. Freedman et al. found that ester yields were significantly reduced if the reactants did not meet these requirements. Sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, which diminished their effectiveness [69]. The effects of FFA and water on transesterification of beef tallow with methanol were investigated by Ma and Hanna [66]. The results showed that the water content of beef tallow should be kept below 0.06% w/w and free fatty acid content of beef tallow should be kept below 0.5%, w/w in order to get the best conversion. Water content was a more critical variable in the transesterification process than FFA [66].

4.2. Properties of biodiesel

The properties of some of the biodiesel fuels are compared in Table 7. The characteristics of biodiesel are close to mineral diesel, and, therefore, biodiesel becomes a strong candidate to replace the mineral diesel if the need arises. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-thirds that of the triglycerides, the viscosity by a factor of about eight and increases the volatility marginally. Biodiesel has viscosity close to mineral diesel. These vegetable oil esters contain 10–11% oxygen by weight, which may encourage combustion than hydrocarbon-based diesel in an engine. The cetane number of biodiesel is around 50. Biodiesel has lower volumetric heating values (about 10%) than mineral diesel but has a high cetane number and flash point. The esters have cloud point and pour points that are 15–25 °C higher than those of mineral diesel [71].

Table 7
Properties of Biodiesel prepared from vegetable oils [64]

Properties	Biodiesel (vegetable oil methyl ester)					
	Peanut	Soyabean	Palm	Sunflower	Linseed	Tallow
Kinematic viscosity at 37.8 °C	4.9	4.5	5.7	4.6	3.59 ^a	—
Cetane number	54	45	62	49	52	—
Lower heating value (MJ/l)	33.6	33.5	33.5	33.5	35.3	—
Cloud point	5	1	13	1	—	12
Pour point	—	−7	—	—	−15	9
Flash point	176	178	164	183	172	96
Density (g/ml)	0.883	0.885	0.88	0.86	0.874	—
Carbon residue (wt%)	—	1.74	—	—	1.83	—

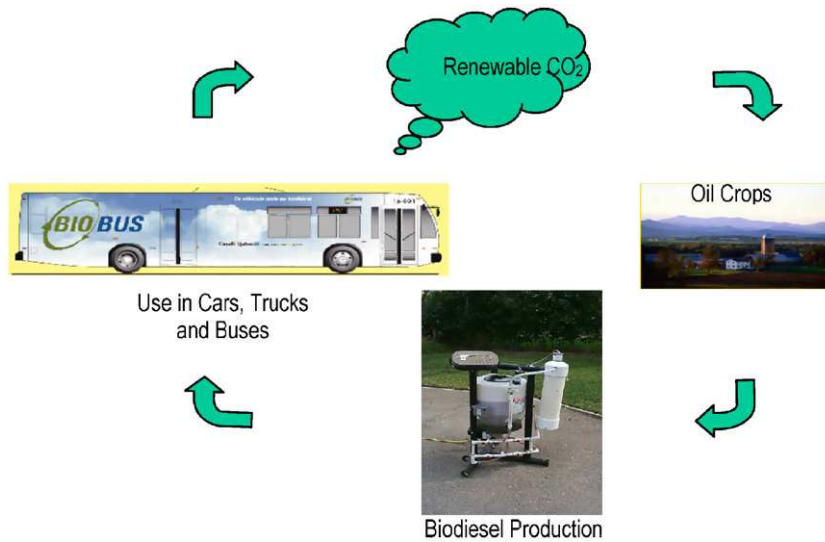
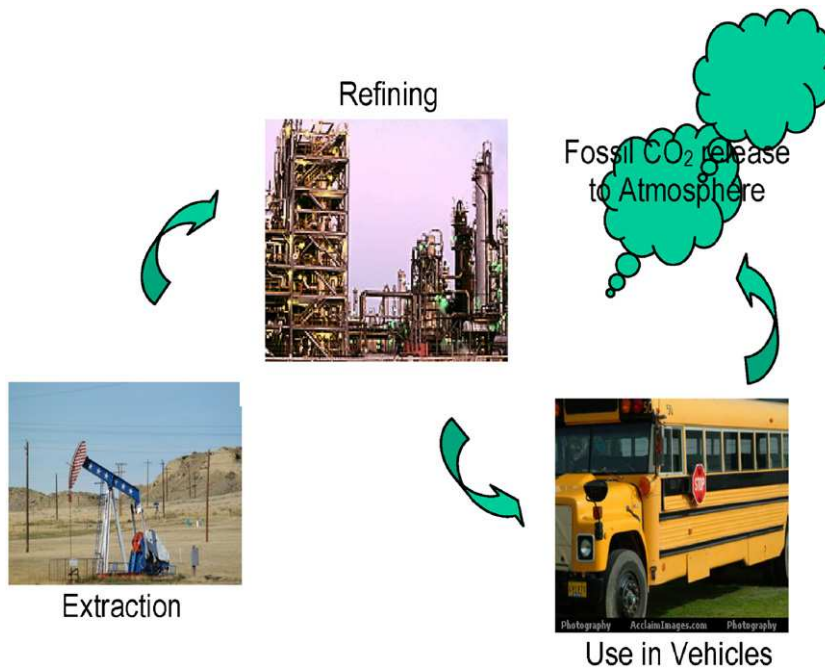
^aAt 40 °C.

4.3. Engine performance characteristics of biodiesel

Biodiesel has low heating value, (10% lower than diesel) on weight basis because of presence of substantial amount of oxygen in the fuel but at the same time biodiesel has a higher specific gravity (0.88) as compared to mineral diesel (0.85) so overall impact is approximately 5% lower energy content per unit volume. Thermal efficiency of an engine operating on biodiesel is generally better than that operating on diesel. Brake-specific energy consumption (bsec) is a more reliable criterion compared to brake-specific fuel consumption (bsfc) for comparing fuels having different calorific values and densities. Several experimental investigations have been carried out by researchers around the world to evaluate the engine performance of different biodiesel blends. Masjuki et al. investigated preheated palm oil methyl esters (POME) in the diesel engine. They observed that by preheating the POME above room temperature, the engine performance, especially the brake power output and exhaust emission characteristics improved significantly [75]. Scholl and Sorenson [76] studied the combustion of soyabean oil methyl ester (SME) in a direct injection diesel engine. They found that most of the relevant combustion parameters for SME such as ignition delay, peak pressure, and rate of pressure rise were close to those observed for diesel combustion at the same engine load, speed, timing and nozzle diameter. They also investigated combustion and emissions characteristics with SME and diesel for different injector orifice diameter. It was found that ignition delay for the two fuels were comparable in magnitude, and the ignition delay of SME was found to be more sensitive to nozzle diameter than diesel. CO emissions from SME were

slightly lower, HC emissions reduced drastically, NO_x for two fuels were comparable and smoke numbers for the SME were lower than that of diesel. Results of their experiments are shown in Figs. 16–19 [76].

Altin et al. investigated the use of sunflower oil, cottonseed oil, soyabean oil and their methyl esters in a single cylinder, four-stroke direct injection diesel engine [62]. The variations of maximum engine torque values in relation with the fuel types are shown in Fig. 20. The maximum torque with diesel operation was 43.1 Nm at 1300 rpm. For ease of comparison, this torque was assumed 100% as reference. The observed maximum torque values of the vegetable oil fuel operations were also at about 1300 rpm but less than the diesel fuel value for each fuel. The variations of maximum engine power values in relation with the fuel types are shown in Fig. 21. The maximum power with diesel fuel operation was 7.45 kW at 1700 rpm. As before, this power was assumed 100% as reference. Observed maximum power values of the vegetable oil fuel operations were also at about 1700 rpm but less than the diesel fuel value for each fuel. These results may also be due to the higher viscosity and lower heating values of vegetable oils. Specific fuel consumption is one of the important parameters of an engine and is defined as the consumption per unit of power in a unit of time. As shown in Fig. 22, the minimum specific fuel consumption values were 245 g/kW/h with mineral diesel, 290 g/kW/h with raw sunflower oil and 289 g/kW/h with opium poppy oil at 1300 rpm. Specific fuel consumption values of the methyl esters were generally less than those of the raw vegetable oils. The higher specific fuel consumption values in the case of vegetable oils are due to their lower energy content. The exhaust

Fig. 15. Biodiesel CO₂ cycle.Fig. 16. Petro-diesel CO₂ cycle.

emissions values for the above investigations are given in Figs. 23–26.

Comparatively lower CO emissions are observed for methyl esters in comparison to raw vegetable oils, due to better spraying qualities. NO₂ emissions are shown in Fig. 24. Highest NO₂ emission was observed from the mineral diesel. As seen in this figure, NO₂ emissions from vegetable oils were

lower than those from mineral diesel, and the NO₂ emission from methyl esters were higher than those of the raw vegetable oils. The most significant factor that causes NO₂ formation is the peak combustion temperature. Since injected fuel droplets of vegetable oils are larger than mineral diesel, the combustion efficiency and maximum combustion temperatures of the vegetable oils were lower and

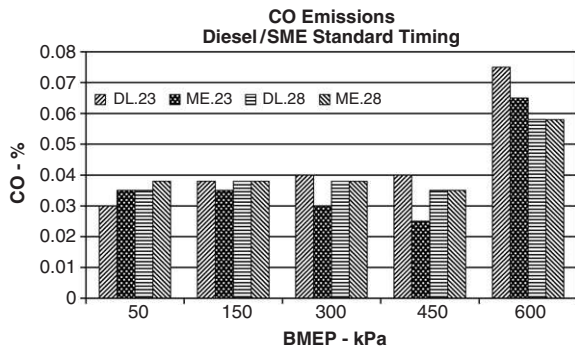


Fig. 17. CO emissions for diesel and SME for two nozzle diameters [76].

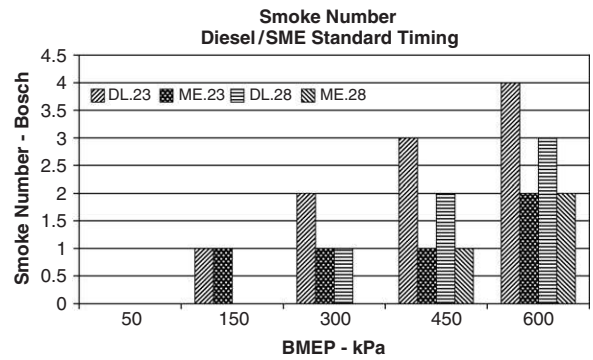


Fig. 20. Smoke emissions for diesel and SME for two nozzle diameters [76].

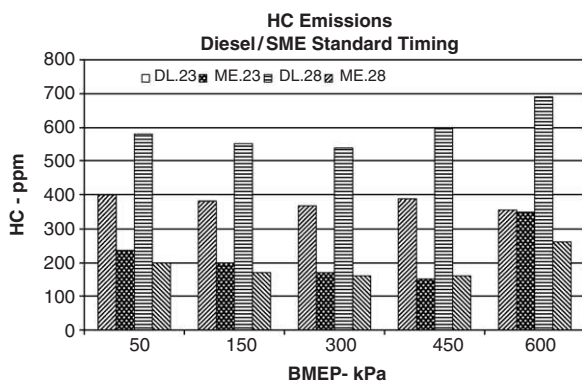


Fig. 18. HC emissions for diesel and SME for two nozzle diameters [76].

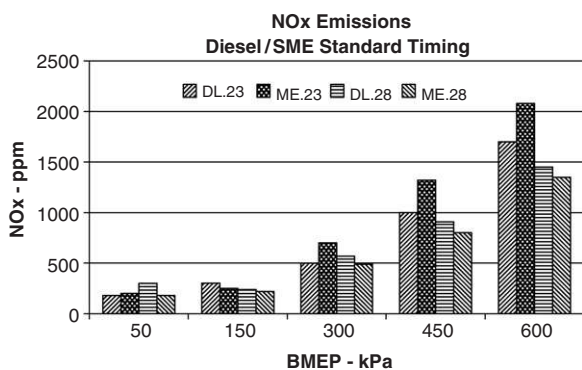


Fig. 19. NO_x emissions for diesel and SME for two nozzle diameters [76].

hence NO₂ emissions were less. The variations of exhaust smoke opacity in (%) for those fuels are shown in Fig. 26. Smoke opacity during each of the vegetable oil operations were greater than that of diesel. The minimum smoke opacity was with diesel. The opacity values of the methyl esters were

between those of diesel and raw vegetable oils. The greater smoke opacity of vegetable oil fuels are mainly due to emission of heavier molecules of hydrocarbons and particulate. Murayma et al. [74] used waste vegetable oil esters in a DI and IDI diesel engine and found that engine performance characteristics were almost same with light oil. Agarwal et al. [70,71] transesterified Linseed oil and prepared Linseed oil methyl ester (LOME) and performed the engine experiments with different blends of biodiesel (LOME) and diesel and compared the results with base line data for diesel using a single cylinder DI diesel engine. Some of the results are given in Figs. 27–32.

Higher thermal efficiencies, lower bsfc and higher exhaust temperatures are reported for all blends of biodiesel compared to mineral diesel. The emission of NO_x increased by 5% for B20 blend. B20 was found to be the optimum biodiesel blend giving maximum increase in thermal efficiency, lowest bsec and advantage in terms of lower emissions [71].

4.4. Engine emissions from biodiesel

Since biodiesel is free from sulfur hence less sulfate emissions and particulate reduction is reported in the exhaust. Due to near absence of sulfur in biodiesel, it helps reduce the problem of acid rain due to transportation fuels. The lack of aromatic hydrocarbon (benzene, toluene etc.) in biodiesel reduces unregulated emissions as well like ketone, benzene etc. Breathing particulate has been found to be hazard for human health, especially in terms of respiratory system problem. PM consists of elemental carbon ($\cong 31\%$), sulfates and moisture ($\cong 14\%$), unburnt fuel ($\cong 7\%$), unburnt lubricating oil ($\cong 40\%$) and remaining may be metals and

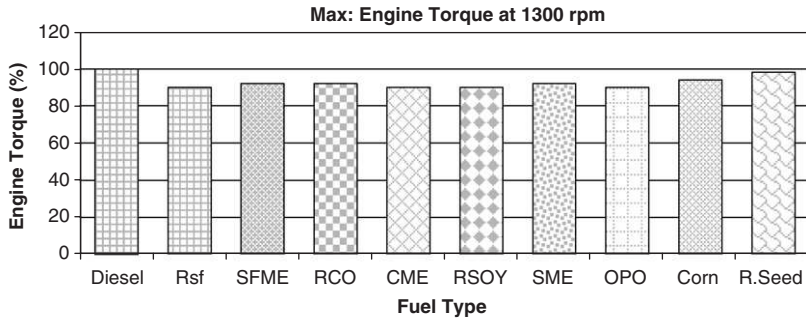


Fig. 21. The variation of engine torque in relation with the fuel types [62].

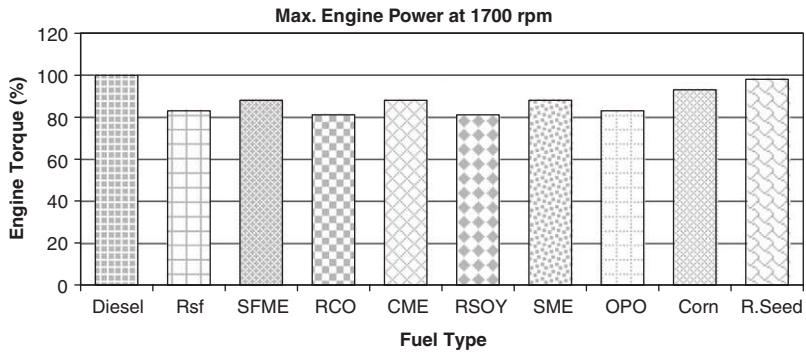


Fig. 22. The variation of engine power in relation with the fuel types [62].

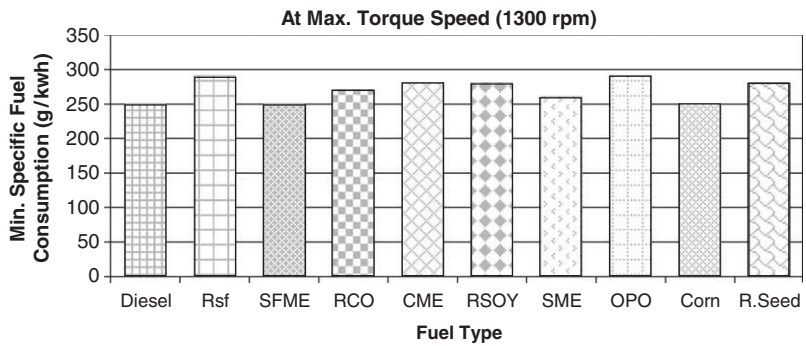


Fig. 23. The variation of minimum specific fuel consumption in relation with the fuel types [62].

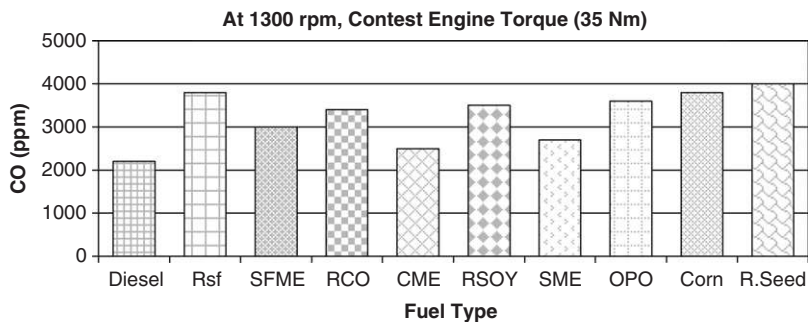


Fig. 24. The variation of CO emissions in relation with the fuel types [62].

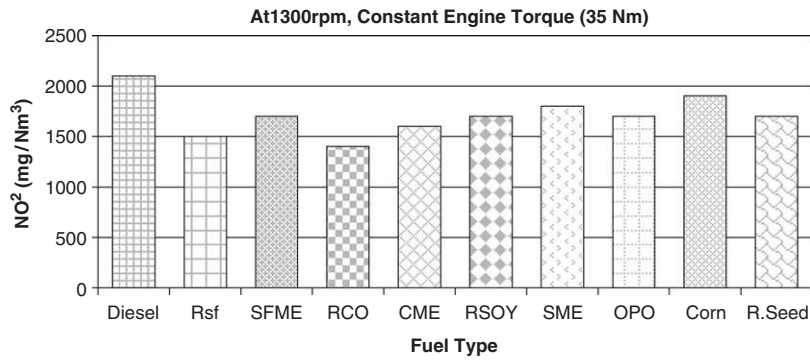


Fig. 25. The variation of NO₂ emissions in relation with the fuel types [62].

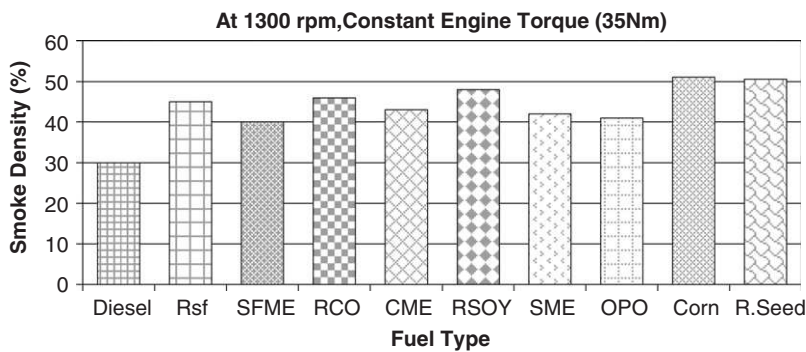


Fig. 26. The variation of smoke density in relation with the fuel types [62].

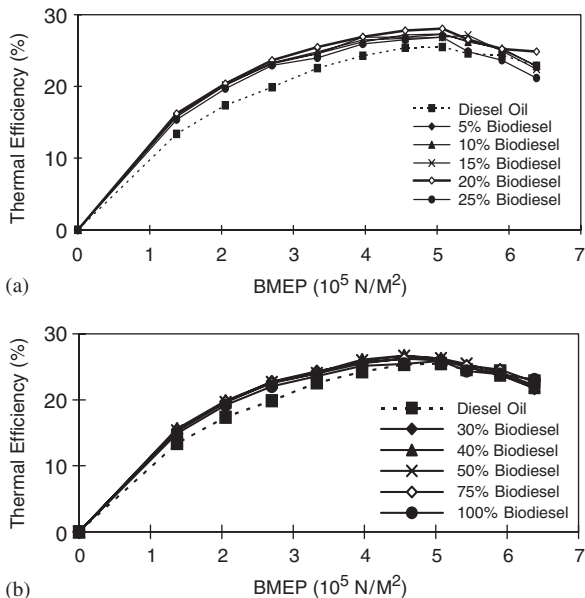
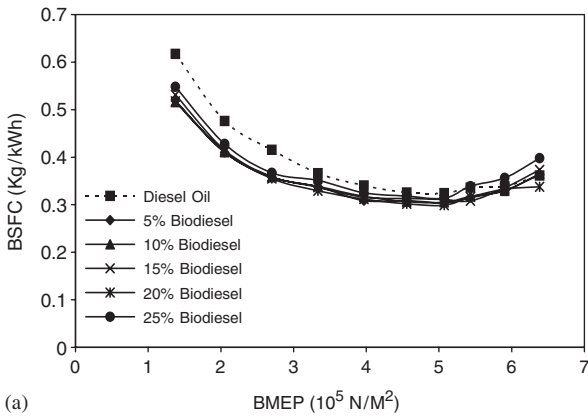


Fig. 27. (a) Comparison of thermal efficiency vs. BMEP curves for lower concentrations of biodiesel and (b) comparison of thermal efficiency vs. BMEP curves for higher concentrations of biodiesel blend.

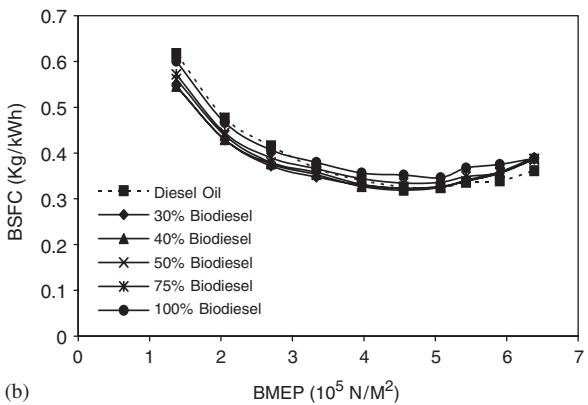
others substances. The typical composition of PM is shown in the Fig. 33.

Biodiesel is oxygenated fuel (hence more complete combustion) and causes lesser particulate formation and emission. Smoke opacity is a direct measure of smoke and soot. Various studies show that smoke opacity for biodiesel is generally lower [70,71,76,77]. Several experimental investigations are performed on 4-stroke DI diesel engines with vegetable oil methyl esters and found that hydrocarbon emissions are much lower in case of biodiesel compared to diesel. This is also due to oxygenated nature of biodiesel where more oxygen is available for burning and reducing hydrocarbon emissions in the exhaust [75–77].

CO is a toxic combustion product resulting from incomplete combustion of hydrocarbons. In presence of sufficient oxygen, CO is converted into CO₂. Biodiesel is an oxygenated fuel and leads to more complete combustion, hence CO emissions reduce in the exhaust. Altin et al. [62], reported that CO emission for biodiesel is marginally higher in comparison to diesel, (Fig. 23), while Scholl et al.

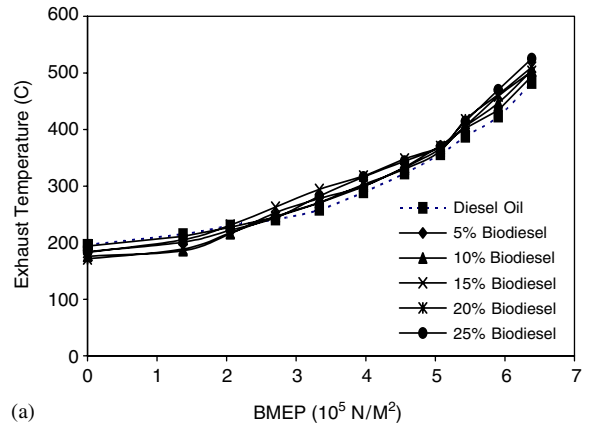


(a)

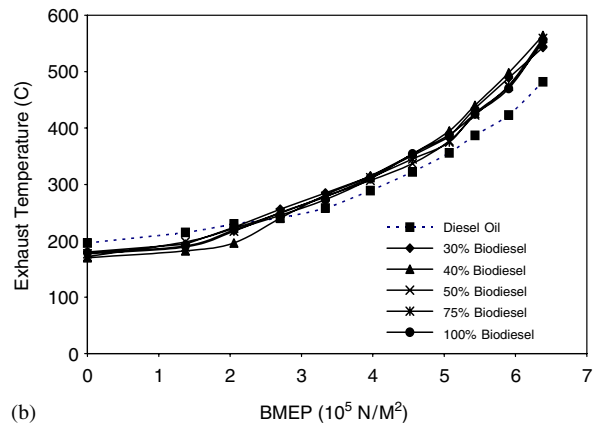


(b)

Fig. 28. (a) Comparison of BSFC vs. BMEP curves for lower concentrations of biodiesel blend and (b) comparison of BSFC vs. BMEP curves for higher concentration of biodiesel blend.



(a)



(b)

Fig. 30. (a) Comparison of exhaust temperature vs. BMEP curves for lower concentrations of biodiesel and (b) comparison of exhaust temperature vs. BMEP curves for higher concentrations of biodiesel blend.

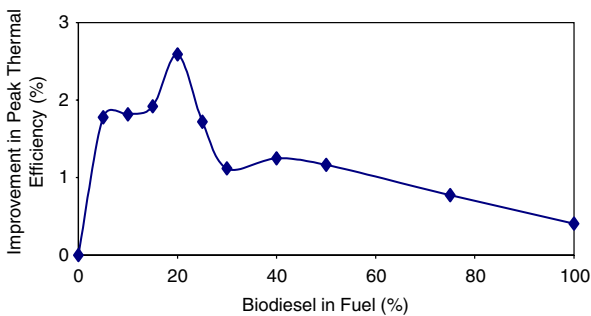


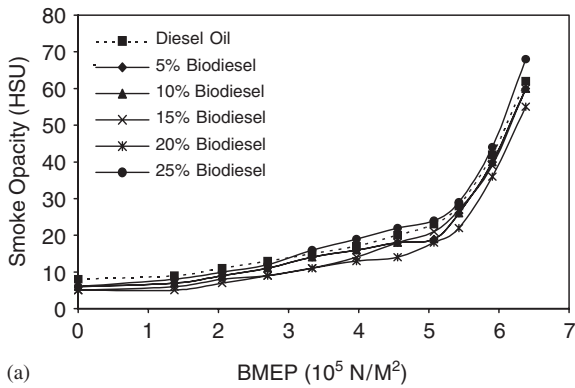
Fig. 29. Improvement in peak thermal efficiency vs. concentration of biodiesel blend curve.

[76] reported the reverse i.e. CO emissions for SME is slightly lower than diesel (Fig. 16). Kalligerous et al. [77] also reported lower CO emissions for sunflower oil.

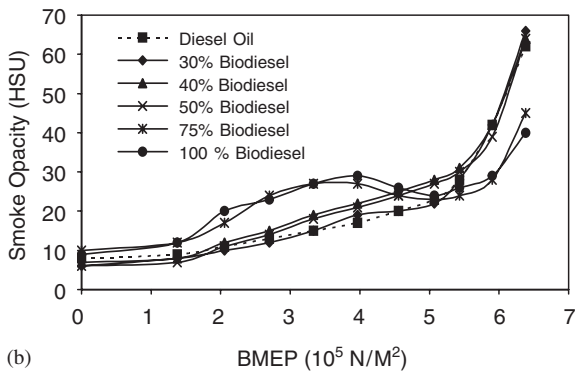
The NO_x forms by oxidation of atmospheric nitrogen at sufficiently high temperatures. Kinetics

of NO_x formation is governed by Zeldovich mechanism, and its formation is highly dependent on temperature and availability of oxygen. There are several reported results [71,76] of slight increase in NO_x emissions for biodiesel. It is quite obvious, that with biodiesel, due to improved combustion, the temperature in the combustion chamber can be expected to be higher and higher amount of oxygen is also present, leading to formation of higher quantity of NO_x in biodiesel-fueled engines. However, biodiesel's lower sulfur content allows the use of NO_x control technologies that cannot be otherwise used with conventional diesel. Hence biodiesel's fuel NO_x emissions can be effectively managed and eliminated by engine optimization. Some result on unmodified Cummins N14 diesel engine on pollutant reduction is shown in Table 8.

Biodiesel use also shows reduction in PAH's, which are identified as carcinogen compounds, so it



(a)



(b)

Fig. 31. (a) Comparison of smoke opacity vs. BMEP curves for lower concentrations of biodiesel blend and (b) comparison of smoke opacity vs. BMEP curves for higher concentrations of biodiesel blend.

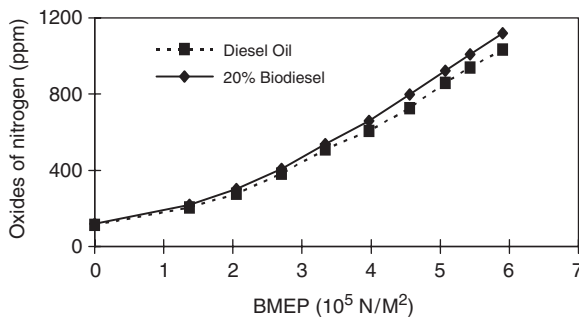


Fig. 32. Concentration of oxides of nitrogen vs. BMEP.

reduces health risks also. A 1998 biodiesel life cycle study, jointly sponsored by the US department of energy and the US department of agriculture, concluded that biodiesel reduces net CO₂ emissions by 78% compared to mineral diesel. This is due to biodiesel's closed carbon cycle. The CO₂ is released into atmosphere, when biodiesel is burned and is recycled by growing plants, which are later pro-

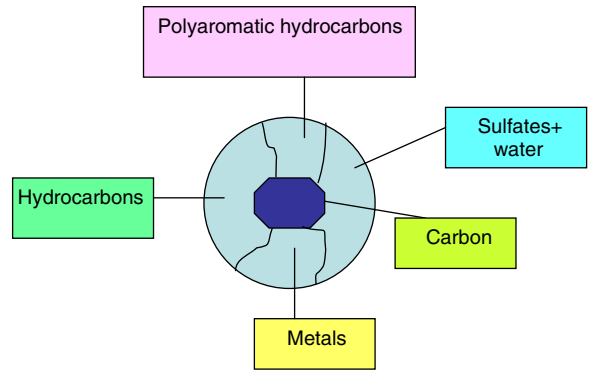


Fig. 33. Typical composition of particulate matter.

Table 8
Biodiesel emissions compared to conventional diesel (ref: www.epa.gov/otaq/models/biodsl.htm)

Emission type	B100 (%)	B20 (%)
Regulated		
Hydrocarbon	-93	-30
Carbon monoxide	-50	-20
Particulate matter	-30	-22
NO _x	+13	+2
Non-regulated		
Sulfates	-100	-20
PAH (polycyclic aromatic hydrocarbons)	-80	-13
Ozone potential of speciated HC	-50	-10

cessed into fuel. Hence, biodiesel also helps mitigate global warming. Peterson et al. [71] also reported that CO₂ emissions are significantly lower with biodiesel.

5. Combustion characteristics of biodiesel

Zhang et al. [78], investigated the combustion characteristics of turbocharged direct injection diesel engine using blends of methyl, isopropyl and winterized methyl ester of soybean oil with diesel as a fuel. They found that all fuel blends except isopropyl ester had similar combustion behavior. Ignition delay for ester/diesel blend was shorter than diesel as a fuel. Senatore et al. [79] found that with rapeseed oil methyl ester heat release always takes place in advance as compared to diesel and injection also starts earlier in case of biodiesel as a fuel and average cylinder gas temperature was higher in case of biodiesel as a fuel. McDonald et al. [80] investigated soybean oil methyl ester as a

fuel on a caterpillar indirect injection diesel engine and found that overall combustion characteristics were quite similar as for diesel except shorter ignition delay for soybean methyl ester. Kumar et al. [81] found that for Jatropha oil methyl ester, ignition delay was higher as compared to ignition delay for diesel as a fuel on a constant speed diesel engine. Selim et al. [82] tested jojoba oil methyl ester (JME) as a fuel on Ricardo compression swirl diesel engine and found that the pressures and pressure rise rates for JME are almost similar to that as gas oil. JME, however, exhibits slightly lower pressure rise rate than gas oil, and JME seems to have slightly delayed combustion.

Experimental investigations have been carried out by Sinha and Agarwal [83] to examine the combustion characteristics in a direct injection transportation diesel engine running with diesel, biodiesel (rice bran oil methyl ester) blend. A Mahindra & Mahindra make four cylinder direct injection diesel engine was instrumented for measurement of combustion pressure, rate of pressure rise and other in-cylinder parameters such as rate of instantaneous heat release, cumulative heat release rate, mass fraction burned etc. Tests were performed at different loads ranging from no load to 100% rated load, at constant engine speed. A careful analysis of heat release and other combustion parameters has been done, which gives precise information about the combustion process, when using biodiesel.

In a CI engine, cylinder pressure depends on the burned fuel fraction during the premixed burning phase, i.e., initial stage of combustion. Cylinder pressure characterizes the ability of the fuel to mix well with air and burn. High peak pressure and maximum rate of pressure rise correspond to large amount of fuel burned in premixed combustion stage. The cylinder pressure crank angle history is obtained at different loads for diesel and B20. Peak pressure and maximum rate of pressure rise are obtained at different loads from these measurements.

Figs. 34–36 show the P - θ diagram for both fuels at different loads. From these figures it is clear that peak pressure increases as the load increases and for B20, fuel combustion starts earlier in comparison to mineral diesel.

Figs. 37 and 38 show that peak pressure and rate of pressure rise are higher for B20 at low engine loads (up to 10% load) but becomes lower when the engine load is increased. However, the change in pressure is not significant. The crank angle where

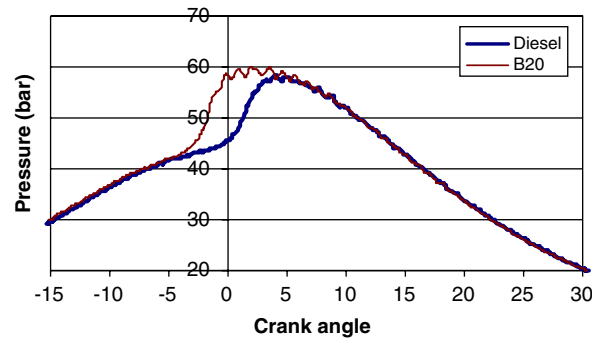


Fig. 34. P - θ diagram at no load, 1400 rpm for medium duty DI transportation engine [83].

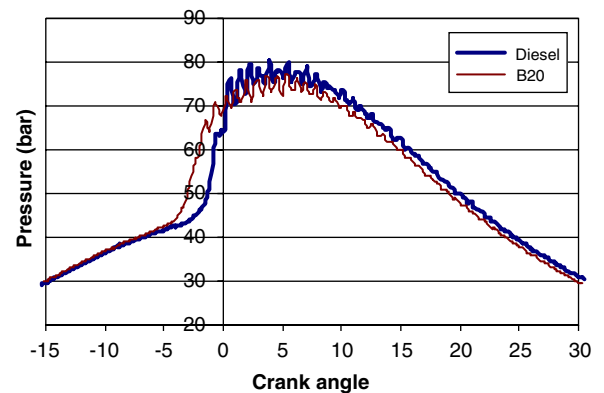


Fig. 35. P - θ diagram at 50% load, 1400 rpm for medium duty DI transportation engine [83].

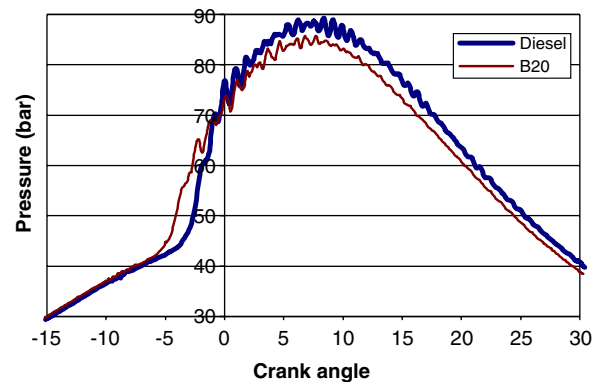


Fig. 36. P - θ diagram at 100% load, 1400 rpm for medium duty DI transportation engine [83].

the peak pressure occurs is shown in Fig. 39. It shows that maximum pressure occurs within the range of 2–7 crank angle degrees after top dead center for both fuels at all loads. Pressure reaches its maximum somewhat later for B20 at higher loads

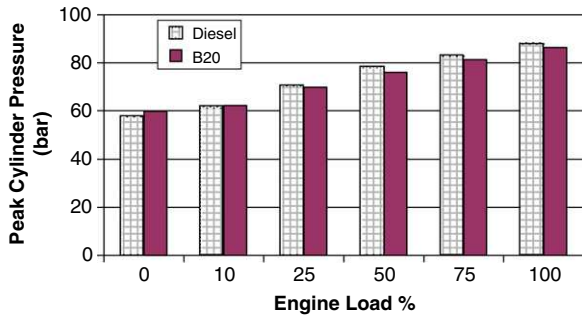


Fig. 37. Variation of peak cylinder pressure with engine load (at 1400 rpm) for medium duty DI transportation engine [83].

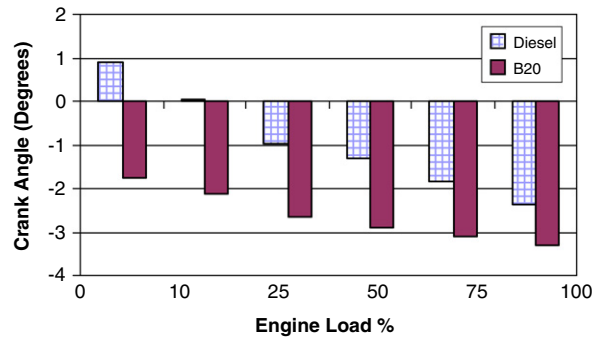


Fig. 40. Crank angle for 10% mass burn for medium duty DI transportation engine [83].

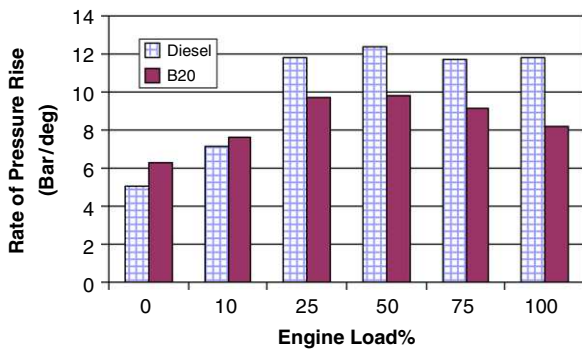


Fig. 38. Variation of rate of pressure rise with engine load (at 1400 rpm) for medium duty DI transportation engine [83].

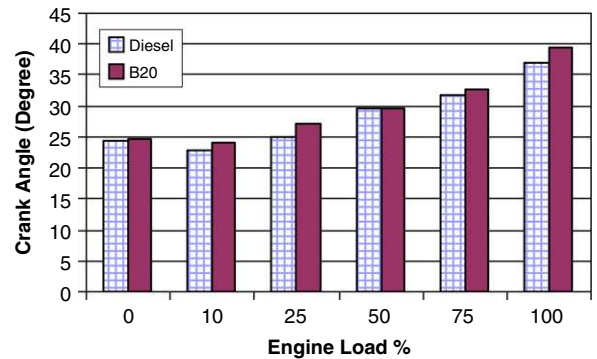


Fig. 41. Crank angle for 90% mass burn for medium duty DI transportation engine [83].

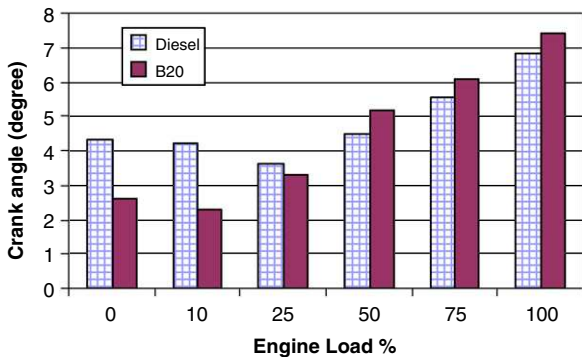


Fig. 39. Crank angle for peak cylinder pressure for medium duty DI transportation engine [83].

which reconfirm that rate of pressure rise is lower at higher loads for B20.

Fig. 40 shows the crank angle at which 10% mass of fuel is burned. This figure shows that 10% of fuel burns earlier for the biodiesel blend. Fig. 41 shows the crank angle at which 90% mass of the fuel is burned. This figure shows that 90% of the fuel is burned earlier in case of diesel, showing faster burn

rate for mineral diesel. This observation substantiates the results in Fig. 38. Increase in combustion duration is due to slow combustion of the injected fuel. Combustion duration for both the fuels increases as the load is increased due to increase in the quantity of fuel injected.

Figs. 42 and 43 show the heat release rate diagrams for both fuels at half and full engine loads. Both fuels experience rapid premixed burning followed by a diffusion combustion as is typical for naturally aspirated engines. After the ignition delay period, the premixed fuel air mixture burns rapidly releasing heat at a very rapid rate, after which diffusion combustion takes place, where the burning rate is controlled by the availability of combustible fuel–air mixture. By analyzing these diagrams, it can be observed that when engine is fueled with B20, the combustion starts earlier under all operating conditions and also B20 shows shorter ignition delay compared to mineral diesel. The premixed combustion heat release is higher for diesel, which is

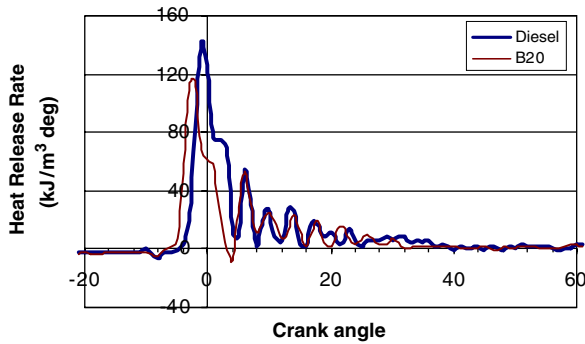


Fig. 42. Heat release rate for 50% engine load, 1400 rpm for medium duty DI transportation engine [83].

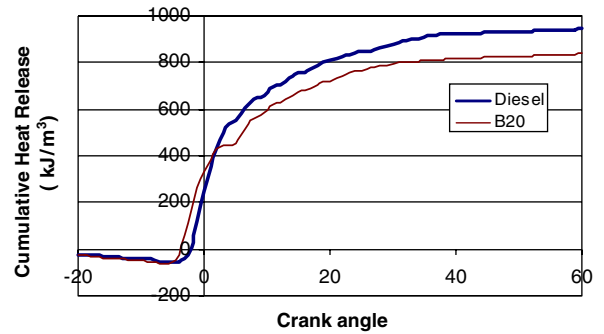


Fig. 45. Cumulative heat release at 50% engine load for medium duty DI transportation engine [83].

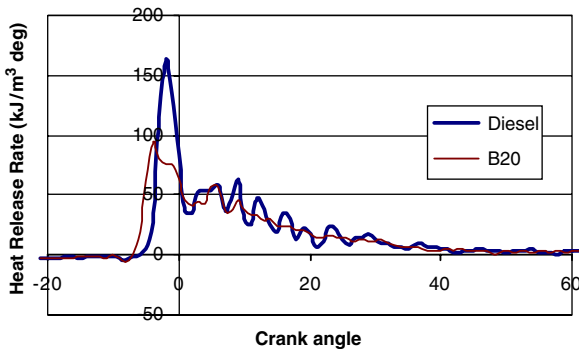


Fig. 43. Heat release rate for 100% engine load for medium duty DI transportation engine [83].

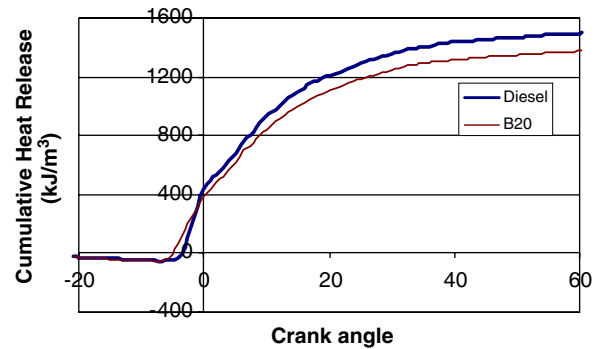


Fig. 46. Cumulative heat release at 100% engine load for medium duty DI transportation engine [83].

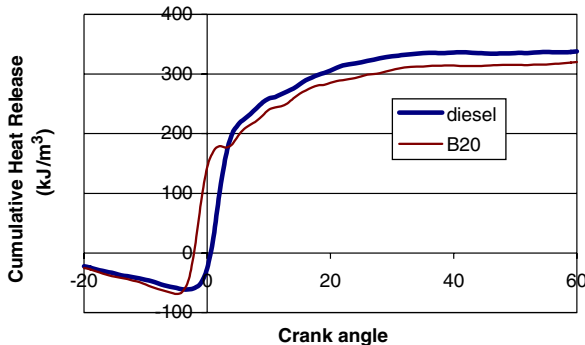


Fig. 44. Cumulative heat release at no engine load for medium duty DI transportation engine [83].

responsible for higher peak pressure and higher rates of pressure rise.

Figs. 44–46 show the cumulative heat release for both fuels at different engine loads. These diagrams again reconfirm early onset of heat release for biodiesel blend. Cumulative heat release is also lower for biodiesel blend compared to mineral diesel

possibly because of lower calorific value of biodiesel blend [84]. The experimental investigations revealed that the overall combustion characteristics were quite similar for biodiesel blend (B20) and mineral diesel. However, combustion starts earlier in case of B20. Ignition delay is lower and combustion duration is slightly longer for B20 compared to mineral diesel. Lower heat release rates were found for B20 as compared to diesel during premixed combustion phase. Total heat release is lower in case of B20 in comparison to mineral diesel. Twenty percent blend of rice bran oil methyl ester did not cause any fuel/combustion related problems [83].

6. Engine tribology investigations of biodiesel

Sliding contact between metallic components of any mechanical system is always accompanied by wear, which results in the generation of minute particles of metal. In diesel engines, the components that are normally subjected to the wear process are piston, piston ring, cylinder liner, bearing,

crankshaft, tappet and valves. In a lubrication system, wear particles remain in suspension in the oil. By analyzing and examining the variations in the concentration of the metallic particle in the lubricant oil after certain running duration, sufficient information about wear rate, source of element and engine condition can be predicted.

Agarwal et al. [85–86] carried out detailed investigations to assess the wear of engine parts using biodiesel fuel. They investigated effect of long-term engine operation on engine wear for a blend of 20% LOME and diesel, both by physical dimensioning and lubricating oil analysis. Two similar new engines were completely disassembled and subjected to dimensioning of various parts and then subjected to long term endurance test on 20% biodiesel blend and mineral diesel, respectively. During this test, each engine was run for 32 cycles (each of 16 h continuous running) at rated speed. The test cycle followed is given in Table 9 (as per IS: 10000, part viii, 1980). The lubricating oil sample were collected from the engines after every 128 h for conducting oil tribological studies. After completion of test, both engines were disassembled for physical inspection and wear measurements of vital parts.

6.1. Carbon deposits

Deposit formations on cylinder head, piston top and injector tip were investigated. Fig. 47 shows carbon deposits on cylinder head, piston top and injector tip of diesel-fueled engine and Fig. 48 shows the same for biodiesel fueled engine. It can be clearly noticed that the carbon deposits for biodiesel-fueled engines are substantially lower than diesel-fueled engine. The piston deposits were scrapped and were weighed and it was found that deposits in the case of biodiesel-fueled engine were 40% less compared to diesel-fueled engine. Carbonization of biodiesel injector after 512 h of opera-

tion was far less than the diesel injector after 200 h of engine operation. This proved that the problem of carbon deposits and coking of injector tip have reduced after transesterification [85].

6.2. Physical wear measurement

The dimensions of the vital parts (bore, rings, and different bearings etc.) were noted before the commencement of and after the completion of long-term endurance test. Wear was measured by accurate measurement of dimensions of various parts. It was observed that the wear of vital moving parts of 20% biodiesel-operated engine was about 30% lower compared to the neat diesel-operated engine [88].

6.2.1. Wear debris measurement through lubricating oil analysis

Oil used for the lubrication of the engine picks up the wear debris of various metals. The quantitative evaluation of wear particles present in oil gives the magnitude of engine component deterioration while qualitative analysis indicates its origin.

6.2.2. Viscosity

Viscosity is the most important property of lubricating oil, as it affects the wear rate of engine components [89]. Very high viscosity lubricating oils increase the frictional loss through the shearing forces of the lubricant preventing the formation of a protective film. During engine operation at normal temperature, a small amount of fuel normally dilutes the lubricating oil, which passes on to the oil sump thru blow-by losses. Engine cold-starting, rich fuel–air mixtures and low ambient temperatures promote fuel dilution of lubricating oil. High fuel dilution reduces oil viscosity, pour point, ash point and diminishes oil's load-carrying ability.

Changes in the lubricant viscosity is undesirable in an engine 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”. 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.

Table 9
Test cycle for long-term endurance test [87]

Load (% of rated load)	Running time (H)
100	4
50	4
110	1
No load (idling)	0.5
100	3
50	3.5

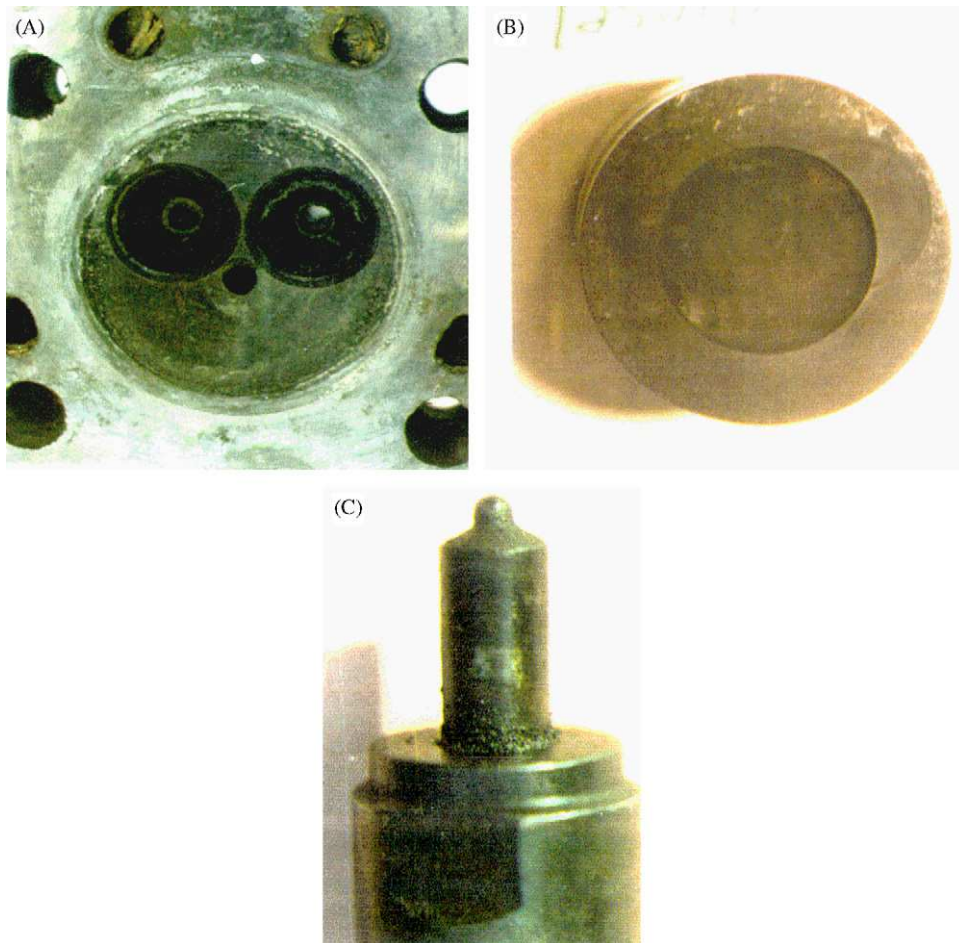


Fig. 47. Carbon deposits on (A) cylinder head of diesel-fueled engine after 512 h of engine operation [85], (B) Piston top of diesel-fueled engine after 512 h of engine operation [85] and (C) injector tip of diesel-fueled engine after 200 h of engine operation [85].

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. If the first factor is dominating and the possibility of fuel dilution is negligible, then the viscosity increases. Sometimes viscosity can decrease, if fuel dilution is a dominating mechanism. The viscosity of all lube oil samples were evaluated at 40 and 100 °C using Setavis kinematic viscometer. The experimental results at these temperatures are shown in Figs. 49 and 50, respectively.

An important observation was that the extent of lowering of viscosity of the lube oil is lesser in case

of biodiesel-fueled system compared to diesel-fueled 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. Relatively higher 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.

The subtle point in this viscosity behavior, however, cannot be neglected. As already discussed, the rate of change of viscosity is also controlled by another mechanisms, viz., fuel dilution, polymerisation and oil oxidation. In this case, it is also possible

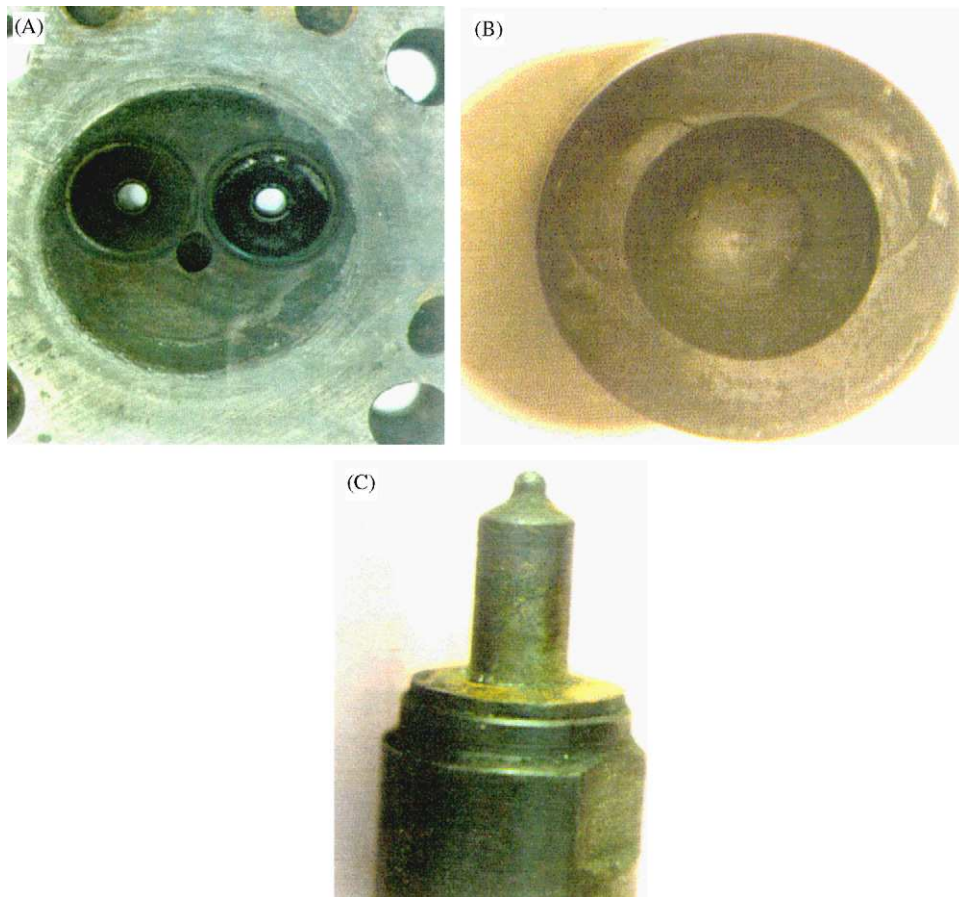


Fig. 48. Carbon deposits on (A) cylinder head of 20% biodiesel-fueled engine after 512 h of engine operation [85], (B) piston top of 20% biodiesel fueled engine after 512 h of engine operation [85] and (C) injector ip of 20% biodiesel-fueled engine after 512 h of engine operation [85].

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 [90]. This fact was supported by FTIR studies, showing higher oxidation of base-stock in case of biodiesel-fueled engine oil as explained in subsequent research work [88].

6.2.3. Ash content

The lubricating oil samples were kept in the furnace at 450 °C for 4 h and then 650 °C for 2 h to produce ash. The residual ash contains the wear debris. The data on ash content in the lubricating oils for biodiesel and diesel fueled CI engine are shown in Fig. 51, it was found that ash content for 20% biodiesel operated engine oil has a lower amount than diesel operated engine oil, it shows

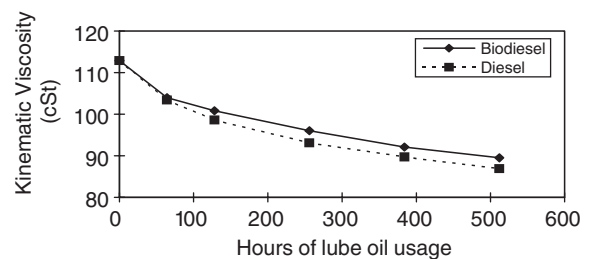


Fig. 49. Kinematic viscosity at 40 °C vs. hours of lube oil usage [90].

that biodiesel fueled engine produced lower amount of wear debris [81].

6.2.4. Atomic absorption spectroscopy

Concentration of various metal present in the lubricating oil sample can be evaluated by atomic absorption spectroscopy (AAS) for quantitative and

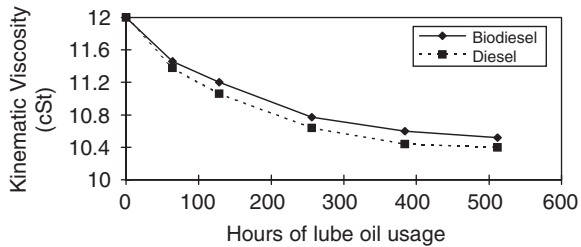


Fig. 50. Kinematic viscosity at 100 °C vs. hours of lube oil usage [90].

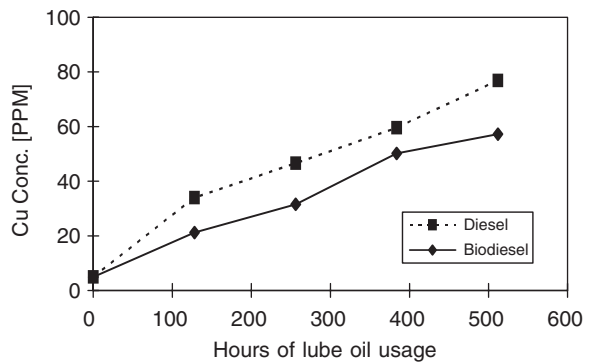


Fig. 53. Copper concentration as a function of lube oil usage [85].

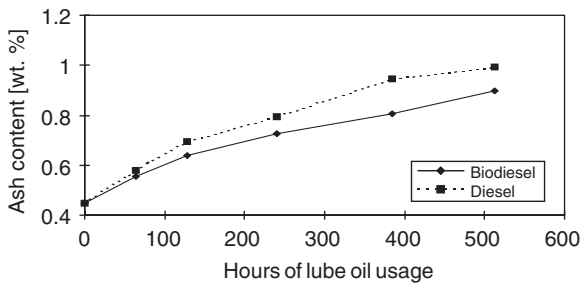


Fig. 51. Ash content vs. hours of lube oil usage [90].

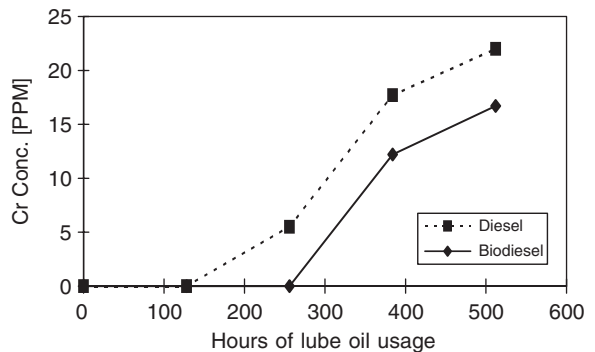


Fig. 54. Chromium concentration as a function of lube oil usage [85].

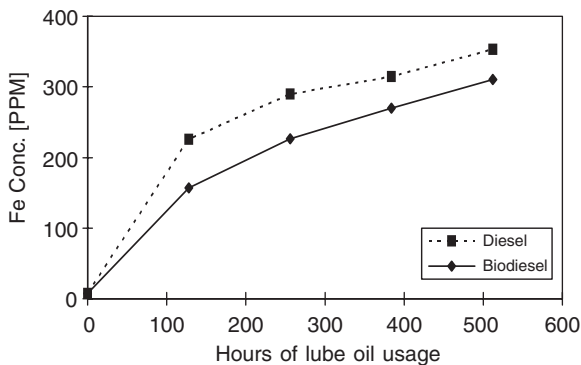


Fig. 52. Iron concentration as a function of lube oil usage [85].

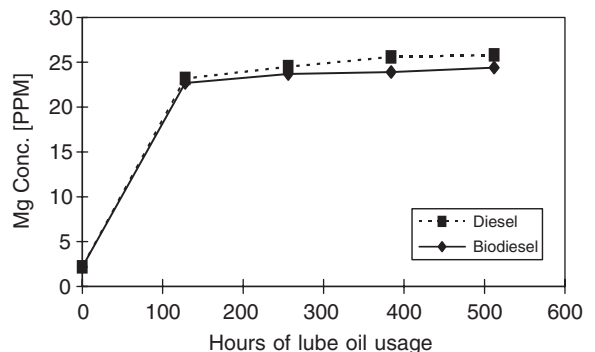


Fig. 55. Magnesium concentration as a function of lube oil usage [85].

qualitative analysis. AAS works on the principle of absorption of a certain wavelength by a particular atomic element. In AAS, a beam of specific wavelength radiation is projected through a pure flame (air–acetylene) on to a photo sensor and the amount of radiation arriving at the photo sensor is recorded. The fluid sample is introduced into the flame and vaporized. The amount of radiation arriving at the photo sensor is reduced in proportion to the quantity of the specific element present in the sample. Wear metal analysis using AAS of lubricat-

ing oil samples drawn from biodiesel (B20) and diesel engines was carried out by Agarwal [85,88] and the results are shown in Figs. 52–58. It is obvious from all these results that the biodiesel-fueled engine leads to lesser wear of engine moving

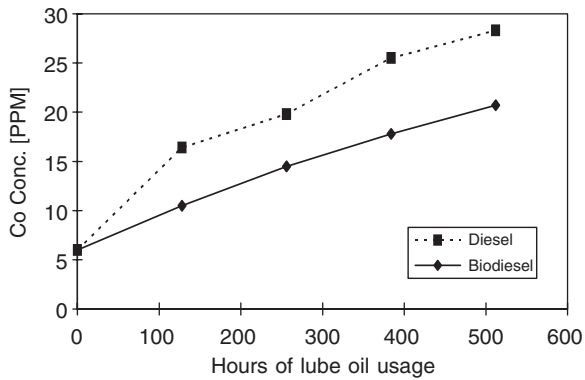


Fig. 56. Cobalt concentration as a function of lube oil usage [85].

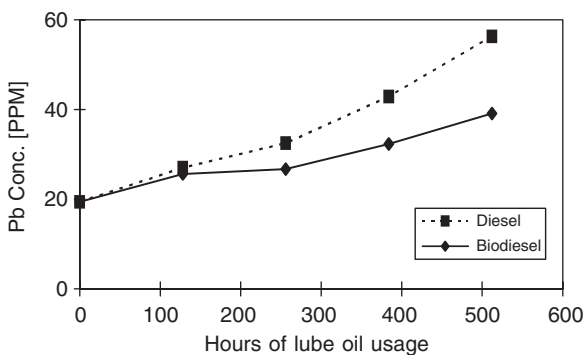


Fig. 57. Lead concentration as function of lube oil usage [85].

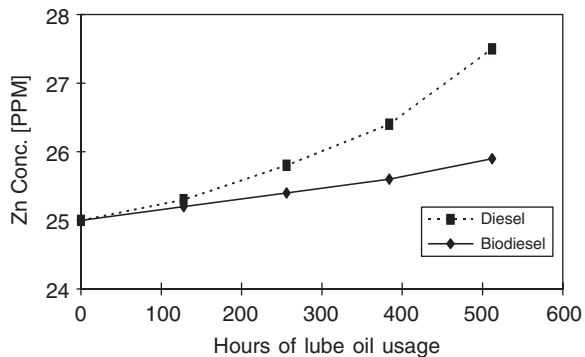


Fig. 58. Zinc concentration as a function of lube oil usage [85].

parts in terms of lesser amount of metallic debris, originated from the different moving parts [85–86].

Oil analysis studies proved to be a powerful tool to estimate not only the condition of the engines, but of other moving parts as well. Moreover, these tests provided valuable and relevant information on the effect of fuel chemistry on the lubricating oil system. Ash content, (Fig. 51) which mainly represents wear debris, was found to be lesser in the case of 20%

biodiesel-fueled system. One of the most interesting studies conducted on the lube oils was for the estimation of individual wear of engine vital parts such as, piston, piston rings, cylinder liner, etc. Atomic absorption spectroscopy studies on lube oils indicated that biodiesel fuel led to lesser wear of engine moving parts in terms of lesser amount of metallic debris (such as Fe, Cu, Zn, Mg, Cr, Pb, and Co) present in lube oil samples [91]. Each element, which is present in oil in the form of wear debris originated from a different moving part. Such an analysis strongly demonstrated that not only the performance characteristics but also wear characteristics of moving parts are better for 20% biodiesel-fueled engine system. The wear of various vital parts reduced up to 30% because of additional lubricity properties of biodiesel. These results of wear measurements by physical methods were also confirmed by AAS. Based on the studies presented, it is concluded that the fuels of bio-origin are superior in wear performance, more environment-friendly, biodegradable, and do not add to global warming problems compared to petroleum based conventional fuels. Biodiesel can be readily adopted as a substitute fuel to the existing diesel engines, which are widely used in the rural agricultural sector worldwide.

7. Economical feasibility of biodiesel

Economical feasibility of biodiesel depends on the price of the crude petroleum and the cost of transporting diesel long distances to remote markets. It is certain that the cost of crude petroleum is bound to increase due to increase in its demand and limited supply. Further, the strict regulations on the aromatics and sulfur contents in diesel will result in higher cost of production of diesel fuels. The cost of producing methyl or ethyl esters from edible oils is currently much more expensive than hydrocarbon-based diesel fuel. Due to the relatively high costs of vegetable oils (about 1.5 to two times the cost of diesel), methyl esters produced from it cannot compete economically with hydrocarbon-based diesel fuels unless granted protection from considerable tax levies applied to the latter. In absence of tax relief, there is a need to explore alternate feedstock for production of biodiesel.

The cost of biodiesel can be reduced if we consider non-edible oils and used-frying oils instead of edible oils. Non-edible oils such as mahua, karanja, babassu, Jatropha, neem etc. are easily available in many parts of the world, and are

cheaper compared to edible oils. Most of these non-edible oils are not used to their potential and in fact produced in surplus quantities. Several countries including Netherlands, Germany, Belgium, Austria, USA, Japan and India discard used frying oils. With the mushrooming of fast food centers and restaurants in the world, it is expected that considerable amounts of used-frying oils will be discarded. This oil can be used for making biodiesel, thus helping to reduce the cost of water treatment in the sewerage system and in the recycling of resources. Before tax, biofuels are currently more expensive than conventional fuels. The explanatory memorandum to the originally proposed biofuels directive states that biodiesel costs approximately €0.50/l to manufacture, while replacing 1 liter of conventional diesel requires 1.1 liter of biodiesel. Mineral Diesel costs (net of tax) approximately €0.20–0.25/l. These figures suggest that pure biodiesel is of the order of 120–175% more expensive [92]. Most of the biodiesel that is currently made, uses soybean oil, methanol and an alkaline catalyst. The high value of soybean oil as a food product makes production of a cost-effective fuel very challenging. However, there are large amounts of low cost oils and fats, such as restaurant waste and animal fats that could be converted to biodiesel. The problem with processing these low-cost oils and fats is that they often contain large amounts of FFA that cannot be converted to biodiesel using an alkaline catalyst [93]. Currently, there are seven producers of biodiesel in the USA. Pure biodiesel (100%) sells for about \$1.50–\$2.00 per gallon before taxes. Fuel taxes will add approximately \$0.50 per gallon. A mix of 20% biodiesel and 80% diesel will cost about 15–20¢ more per gallon over the cost of mineral diesel [94]. The cost of biodiesel production results in a generally accepted view of the industry in Europe that biodiesel production is not profitable without fiscal support from the government.

A review of 12 economic feasibility studies shows that the projected costs for biodiesel from oil seed or animal fats have a range US\$0.30–0.69/l, including meal and glycerin credits and the assumption of reduced capital investment costs by having the crushing and/or esterification facility added onto an existing grain or tallow facility. Rough projections of the cost of biodiesel from vegetable oil and waste grease are, respectively, US\$0.54–0.62/l and US\$0.34–0.42/l. With pre-tax diesel priced at US\$0.18/l in the US and US\$0.20–0.24/l in some European countries, biodiesel is thus currently not

economically feasible, and more research and technological development will be needed [95].

8. Conclusion

Using ethanol as a fuel additive to unleaded gasoline causes an improvement in engine performance and exhaust emissions. Ethanol addition results in an improvement in brake power, brake thermal efficiency, volumetric efficiency and fuel consumption, however the brake specific fuel consumption and equivalence air–fuel ratio decrease because of lower calorific value of the gasohol. Using an ethanol–unleaded gasoline blend leads to a significant reduction in exhaust emissions of CO and HC for all engine speeds. On the other hand, CO₂ emissions increase marginally. Ethanol diesel blends up to 20% can very well be used in present day constant speed CI engines without any hardware modification. Exhaust gas temperatures and lubricating oil temperatures were lower for ethanol diesel blends than mineral diesel. The engine could be started normally both hot and cold. Significant reduction in CO and NO_x emission was observed while using ethanol diesel blends.

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. A continuous transesterification process is a method of choice to lower the production cost. Researchers in various countries carried out experimental research using vegetable oils and biodiesel as petroleum fuel substitutes. Vegetable oil methyl esters gave performance and emission characteristics comparable to that of diesel. 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 gets drastically reduced after esterification. A 20% blend of biodiesel with mineral diesel improved the cetane number of diesel. The calorific value of biodiesel was found to be slightly lower than mineral diesel. All these tests for characterization of biodiesel demonstrated that almost all the important properties of biodiesel are in very close agreement with the mineral diesel making it a potential candidate for the application in CI engines. A diesel engine can perform satisfactorily on biodiesel blends without any engine hardware modifications. Long-term endurance test using biodiesel proved that biodiesel can be used for substituting mineral diesel in long run. The 20% biodiesel blend was found to be

the optimum concentration for biodiesel blend, which improved the peak thermal efficiency of the engine by 2.5%, reduced the exhaust emissions and the brake specific energy consumption substantially. Smoke emissions reduced appreciably as a result of biodiesel utilization in the engine. 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 wear of various vital parts reduced up to 30% because of additional lubricity properties of biodiesel. These results of wear measurements by physical methods were also confirmed by atomic absorption spectroscopy. Oil analysis studies proved to be a powerful tool to estimate not only the condition of the engines, but of other moving parts as well. Ash content, which mainly represents wear debris, was found to be lesser in the case of 20% biodiesel-fueled system. One of the most interesting studies conducted on the lube oils was for the estimation of wear of vital engine parts such as, piston, piston rings, cylinder liner, etc. A detailed experimental analysis for finding out the combustion characteristics of biodiesel blend (B20) vis-à-vis mineral diesel was carried out. The experimental investigations revealed that the overall combustion characteristics were quite similar for biodiesel blend (B20) and mineral diesel. However, combustion starts earlier in case of B20. Ignition delay is lower and combustion duration is slightly longer for B20 compared to mineral diesel. Lower heat release rate were found for B20 as compared to diesel during premixed combustion phase. Total heat release is lower in case of B20 in comparison to mineral diesel. Twenty percent blend of rice bran oil methyl ester did not cause any fuel/combustion related problems. This detailed experimental investigation confirms that biodiesel can substitute mineral diesel without any modification in the engine.

Hence, biodiesel may be considered as diesel fuel substitutes. The use of biofuels as IC engine fuels can play a vital role in helping the developed and developing countries to reduce the environmental impact of fossil fuels.

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