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A REVIEW- Biodiesel Production, and Properties

Rajat Kumar[1], Lokesh Sexana[2], Rajesh Kumar, Ranu Sonkar and Pratima Katiyar[5]
[1,2] Chemistry Department DAV-PG College Kanpur-208001, India
3,4,5 Chemistry Department PEC KANPUR
Corresponding Author Rajat Kumar

Abstract
The work presented in this paper has been carried out using Jatropha seed oil to prepare biodiesel in laboratory by formulating its properties closer to that of diesel fuel. Although biodiesel is prepared from various renewable sources such as vegetable oils and animal fats but here in this project jatropha curcas seed oil was used to produce biodiesel by transesterification process, it's a patent (Belgian patent 422,877) described as the alcoholysis of vegetable oil using methanol and ethanol in order to separate the fatty acids from the glycerol, that accounts for the production of what is known as biodiesel today. Plant species Jatropha curcas is the main commodity source for Biodiesel in India.
Keywords: *Straight vegetable oil, Jatropha oil, Esterification, Transestrification Jatropha oil methyl ester.*

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I. INTRODUCTION

Diesel fuels have an essential function in the industrial economy of a country. These are used in heavy trucks, city transport buses, electric generators, farm equipment, underground mine equipment, etc[1]. Compared to the rest of the world, India's demand for diesel is roughly six times that of gasoline. One hundred years ago, Rudolf diesel tested peanut oil as fuel for his engine for the first time on August 10, 1893. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, usually only in emergency. The first international conference on plant and vegetable oils as fuels was held in Fargo, North Dakota in August 1982. Vegetable oils hold promise as alternative fuels for diesel engines. But their high viscosities, low volatilities and poor cold flow properties have led to the investigation of various derivatives. Fatty acid methyl esters, known as biodiesel, derived from triglycerides by transesterification with methanol have received the most attention.

The name biodiesel was introduced in the united state in 1992 by National Soy Diesel Development Board (has National Biodiesel Board) which pioneered the commercialization of biodiesel in United States. In Aprial 2003, the GOI launched a National Bio-diesel Mission (NBM) identifying jatropha curcus as the most suitable tree-borne oilseed for biodiesel production. The planning Commission of India had set an ambitious target of covering 11.2 to 13.4 million hectares of land under jatropha cultivation by end of 11th five year plan 2011-2012. The Central Government and Several State Government provide fiscal incentives for supporting planting of jatropha and other non-edible oilseeds Fukuda et. al 2001.

Biodiesel can be used in any ratio with petroleum diesel as it has very similar characteristics but give lower exhaust emissions. Apart from this biodiesel have additional properties to such as it is renewable, biodegradable, nontoxic, and essentially free of sulfur and aromatics. Biodiesel fuel has the potential to reduce the level of pollutants and the level of potential or probable carcinogens stated that biodiesel has become more attractive in recent times because of its environmental benefits and fact that it is made from renewable resource. The raw materials being exploited commercially for Biodiesel are the edible fatty oils derived from rapeseed, soybean, palm, sunflower, coconut, and linseed etc.

Estimate indicates that biodiesel could represent as much as 20-22% of all on-road diesel used in Brazil, Europe, China and India by the year 2020. Use of Biodiesel is catching up all over the world especially in developed countries. Rapid economic growth in India and China will significantly increase demand for oil. At present, India is producing only 30% of has total requirement petroleum fuels. India is the fifth largest energy consumer and imported nearly 70% of its crude oil requirement (90 milliontonnes) during 2003-2004, which costs about Rs 80,000 crore every year.[3]

In India it is an astonishing fact that blending of 5% biodiesel fuel to the diesel fuel can save about Rs 4000 crore every year. It is estimated that India will be able to produce 288 metric tonnes of Biodiesel by the end of 2012, which will supplement 41.14% of the total demand of diesel fuel consumption in India. The cost of biodiesel and demand of vegetable oils can be reduced by use of non edible oils instead of vegetable oils but India is not self- sufficient in edible oils.

1.1 Hydrocarbon-Based Diesel Fuels

It is a general property of hydrocarbons that the auto-ignition temperature is higher for more volatile hydrocarbons. Therefore, the less volatile middle distillate fractions of crude oil boiling in the range of 250 to 370°C are suitable as diesel fuels. The hydrocarbons present in the diesel fuels include paraffins, naphthenes, olefins and aromatics. Carban numbers of these hydrocarbans ranges from 12 to 18. Since straight-run diesel fraction from a given crude oil is fixed, varying amounts of selected cracked distillates from conversion processes such as fluid catalytic cracking hydrocracking, coking units are used to increase the volume available for meeting the growing demand of diesel fuels.

Indian requirement of diesel fuels are listed in Table1.The performance problems versus fuel-related causes for compression-ignition (diesel) engines are summarized in Table-2[1]. The more critical problems are those related to combustion, injector nozzle pump fouling and filter plugging.

Table-1
Indian requirement for diesel fuels IS: 1460-1974

SI.No.	Characteristics	Requirement
1	Acidity, inorganic	Nil
2	Acidity, total, mg KOH/g, Max.	0.50
3	Ash, wt. %, Max.	0.01
4	Carbon residue (Ramsbottom), wt.%, Max	0.20
5	Cetane number, Min	42.00[b]
6	Pour point, ° C, Max	6.00[a]
7	Copper strip corrosion for 3 h at 100 ° C	Not worse than No. 1
8	Distillation-recovery at 366 °C, vol. %. Min.	90.00
9	Flash point (Abel), °C, Min.	38.00
10	Kinematic viscosity at 38 ° C, cSt	2.0-7.5
11	Sediment, wt. %,, Max.	0.05
12	Total Sulphur, wt%, Max	1.00
13	Water content, vol.%, Max	0.05

[a] Subject to seasonal changes, pour point varies from 0 to 18 °C
[b] 45 for Naval applications.

Table- 2 Effect of performance of fuel on compression-ignition engine

Performance problem	Probable fuel-related causes
1. Poor combustion, smoking	(a) Low cetane number
	(b) Water contamination
	(c) Improper cloud point
	(d) Lighter/heavier fuel contamination
2. Excess cylinder wear	(a) Fuel dilution
	(b) High Sulphur content
	(c) Dirt (silicon) contamination
3. Injector nozzle plugging/water	(a) Soluble metal contaminants
	(b) Heavy end impurities
	(c) Preformed gum impurities
4. Injector pump fouling sticking	(a) High Sulphur/hetero-atom content
	(b) Gasoline contamination
	(c) Heavy ends contamination
	(d) Low fuel viscosity
5. Filter plugging	(a) Water contamination
	(b) Fuel impurities
	(c) Improper cloud point
	(d) Thermally-reactive hydrocarbons
6. Excess engine deposits	(a) Heavy ends contamination
	(b) Low cetane number
	(c) High sulphur/hetero-atom content

1.1.1 Present Indian Scenario

Fuels are inevitable for industrial development and growth of any country. The life span of fossil fuel resources has always been terrifying. Biodiesel, a renewable source of energy seems to be an ideal solution for global energy demands including India as well. In India it is an astonishing fact that blending of 5% Biodiesel fuel to the diesel fuel can save about Rs 4000 crore every year. It is estimated that India will be able to produce 288 metric tonnes of Biodiesel by the end of 2012, which will supplement 41.14% of the total demand of diesel fuel consumption in India. The cost of Biodiesel and demand of vegetable oils can be reduced non edible oils, instead of vegetable oils but India is not self- sufficient in edible oils.

1.2.2 Environmental Pollution from Diesel Fuels

When biodiesel displaces petroleum, it reduces global warming gas emissions such as carbon dioxide ($_{CO}$). When plants like soybeans grow they take CO_2 the air to make the stems, roots, leaves, and seeds (soybeans). After the oil is extracted from the soybeans, it is converted into biodiesel and when produces CO_2 and other emissions, which return to the atmosphere. This cycle does not add to the net CO_2 concentration in the air because the next soybean crop will reuse the CO_2 in order to grow. When fossil fuels are burned, however, 100% of the CO_2 released ads to the CO_2 concentration levels in the air. Because fossil fuels are used to produce biodiesel, the recycling of CO_2 with biodiesel is not 100%, but substituting biodiesel for petroleum diesel reduces life-cycle CO_2 emission by 78%. B20 reduces CO_2 by 15.66%.Biodiesel reduces tailpipe particulate matter (PM), hydrocarbon (HC), and carbon monoxide (CO) emissions from most modern four-stroke CI engines. These benefits occur because the fuel (B100) contains 11% oxygen by weight. The presence of fuel oxygen allows the fuel to burn more completely, so fewer unburned fuel emissions result. This same phenomenon reduces air toxics, because the air toxics are associated with the unburned or partially burned HC and PM emissions. Testing has shown that PM, HC, and CO reductions are independent of the feedstock used to make biodiesel. The EPA reviewed 80 biodiesel emission tests on CI engines and has concluded that the benefits are real and predictable over a wide range of biodiesel blends. In older two-stroke engines, B20 can reduce CO, HC, and PM if the engines do not consume excessive amounts of lube oil. If lube oil consumption is high, PM benefits from B20 use may be less. In addition, one of the first benefits that people notice when using biodiesel or biodiesel blends is the smell. Using biodiesel can make diesel exhaust smell better; more like cooking odors.

1.2.3 Need for Alternative Fuels.

The alternative diesel fuels must be technically acceptable, economically competitive, environmentally acceptable and easily available. From the viewpoint of these requirements, triglycerides (vegetable oils/animal fats) and their derivatives may be considered as viable alternatives for diesel fuels. Vegetable oils are widely available from a variety of sources, and they are renewable. As far as environmental considerations are concerned, unlike hydrocarbon-based fuels, the Sulphur content of vegetable oils is close to zero and hence, the environmental damage caused by Sulphuric acid is reduced. Moreover, vegetable oils take away more carbon dioxide from the atmosphere during their production than is added to it by their later combustion. Therefore, it alleviates the increasing carbon dioxide content of the atmosphere.

1.2 DIFFERENT SOURCES OF BIODIESEL FUELS

1.3.1 Edible and non-edible oils

Biodiesel can be produced either from edible or non-edible oils. Most of the edible oils are produced from the crop land. The use of edible vegetable oils for bio diesel production has recently been of great concern because they compete with food materials. Disadvantages of using bio diesel produced from agricultural crops involve additional land use, as land area is taken up and various agricultural inputs with their environmental effects are inevitable. Switching to bio diesel on a large scale requires considerable use of our arable area. If the same thing is to happen all over the world, the impact on global food supply could be a major concern. Currently, more than 95% of the world bio-diesel is produced from edible oil which is easily available on large scale from the agricultural industry. However, continuous and large-scale production of biodiesel from edible oil without proper planning may cause negative impact to the world, such as depletion of food supply leading to economic imbalance. A possible solution to overcome this problem is to use non-edible oil. As the demand for edible oils for food has increased tremendously in recent years, it is urgently required to justify the use of these non edible oils for fuel use purposes such as biodiesel production. Moreover, these oils could be less expensive to use as fuel. Hence, the contribution of non-edible oils such as Jatropha and Karanja and Mahua will be significant as a non edible plant oil source for biodiesel production. Several studies have shown that there exists an immense potential for the production of plant based oil to produce biodiesel. Studied the prospects of fatty acid methyl esters (FAME) of some 26 non-traditional plant seed oils including jatropha to use as potential biodiesel in India. Among them, Azadirachta indica, Calophyllum inophyllum, J. curcas and pongamia pinnata were found most suitable for use as biodiesel and they meet the major specification of biodiesel for use in diesel engine. Moreover, they reported that 75 oil bearing plants contain 30% or more oil in their seed, fruit or nut. Reported that there are over 300 different species of trees which produce oil bearing seeds. Thus, there is a significant potential for non-edible oil source from different plants for biodiesel production as an alternative to petro diesel.

1.3.2 FEEDSTOCKS USED FOR BIODIESEL:

Commonly used method for biodiesel production is transesterification of vegetable oils and animal fats. Vegetable oil can be extracted from a variety of plants and their seeds. Whilst a large variety of seeds are extracted, only some of them are of commercial world importance. These include soyabeans, sunflower, ground nuts, castor, cotton seed, olives and rice bran. Oils and fats are composed of molecules called triglycerides. Each triglyceride is composed of fatty acids three long chains fatty acids of 8-22 carbons attached at a glyceride backbone.

Variety of oils can be used to produce biodiesel. These include:

Virgin oil feedstock; rapeseed and soybean oils are most commonly used, soybean oil alone accounting for about ninety percent of all fuel stocks in the US. It also can be obtained from field pennycress and Jatropha other crops such as mustard, flax, sunflower, palm oil. Waste vegetable oil. Animal fats including tallow, lard, yellow grease, chicken fat and the by-products of the production of Omega-3 fatty acids from fish oil. Algae, which can be grown using waste materials such as sewage and without displacing land currently used for food production. Oil from halophytes such as salicornia bigelovii, which can be grown using saltwater in coastal areas where conventional crops cannot be grown, with yields equal to the yields of soybeans and other oilseeds grown using freshwater irrigation.

Many advocates suggest that waste vegetable oil is the best source of oil to produce biodiesel, but since the available supply is drastically less than the amount of petroleum-based fuel that is burned for transportation and home heating in the world; this local solution does not scale well.

Animal fats are a by-product of meat production. Although it would not be efficient to raise animals (or catch fish) simply for their fat, use of the by-product adds value to the livestock industry (hogs, cattle, poultry). However, producing biodiesel with animal fat that would have otherwise been discarded could replace a small percentage of petroleum diesel usage. Today, multi-feedstock biodiesel facilities are producing high quality animal-fat based biodiesel. Currently, a 5-million dollar plant is being built in the USA; with the intent of producing 11.4 million liters (3 million gallons) biodiesel from some of the estimated 1 billion kg (2.3 billion pounds) of chicken fat produced annually the local Tyson poultry plant. Similarly, some small-scale biodiesel factories use waste fish oil as feedstock.

Feedstock for biodiesel is classified based on free fatty acids content:-

- Refined oils such as soybean or canola oil (FFA < 1.5%)
- Low Free Fatty acids oil yellow greases and animal fats (FFA < 4%)
- High Free Fatty acids oils greases, spent frying oils and animals fats (FFA 5% to > 20%)
- Other feed stocks sewage greases and high Free Fatty acids greases (FFA > 50%)

Following Table summarizes the feedstocks used to produce Biodiesel in various countries

Table- 3 Common feed stocks for Biodiesel

Vegetable Oil	Country
Rape seed	France, US
Sunflower	Italy, Southern France
Soybean	USA
Palm	Malaysia
Linseed, Olive	Spain
Cotton Seed	Greece
Jatropha curcas	Nicaragua, India
Used Frying Oils	Australia
Other Waste oils and Fats	USA

1.2 C Feedstocks in Indian context:

For India non- edible oils obtained from plants that can be grown on waste/ semi arid lands are more suitable. Species can be selected based on the regional climatic conditions. Most of the non-edible oils available in India contain high free fatty acids (2-12%). Table provides a list of typical non-edible oils that can be used for producing Biodiesel.

Under Indian condition mainly Jatropha plant can be considered for biodiesel production. Jatropha curcas (Vana Erand*)* gives Jatropha oil, the non-edible vegetable oil used to produce high quality biodiesel for standard diesel car. Jatropha plant can be grown on large scale on wastelands even on gravelly, sandy and saline soils. Climatically, Jatropha plant is found in the tropics and subtropics and likes heat, even in lower temperatures and can withstand a light frost. Its water requirement is extremely low and it can stand long periods of drought by shedding most of its leaves to reduce transpiration loss. Jatropha curcas (Vana Erand) is also suitable for preventing soil erosion and shifting of sand dunes.

A typical analysis of the Jatropha curcas (VanaErand*)* seed shows the following chemical composition:

- Moisture 6.20 %
- Protein 18.00 %
- Fat 38.00 %
- Carbohydrates 17.00 %
- Fiber 15.50 %
- Ash 5.30 %

The oil content is 35 – 40% in the seeds and 50 – 60% in the kernel. The oil contains 21% saturated fatty acids and 79% unsaturated fatty acids. There are some chemical elements in the seed that are poisonous and render the oil not appropriate for human consumption.

This document is a guide for those who blend, distribute, and use biodiesel and biodiesel blends. It is intended to help fleets and individual users, blenders, distributors, and those involved in related activities understand procedures for handling and using biodiesel fuels. We hope it will be a useful tool, both when planning biodiesel use and as an ongoing resource.

Biodiesel is a renewable fuel manufactured from vegetable oils, animal fats, and recycled cooking oils. Biodiesel offers many advantages:

• It is renewable.
• It is energy efficient.
• It displaces petroleum derived diesel fuel.
• It can be used in most diesel equipment with no or only minor modifications.
• It can reduce global warming gas emissions.
• It can reduce tailpipe emissions, including air toxics.
• It is nontoxic, biodegradable, and suitable for sensitive environments.
• It is made in the United States from either agricultural or recycled resources.
• It can be easy to use if you follow these guidelines.

Biodiesel can be used in several different ways. You can use 1% to 2% biodiesel as a lubricity additive, which could be especially important for ultra low sulfur diesel fuels (ULSD, less than 15 ppm sulfur), which may have poor lubricating properties. You can blend 20% biodiesel with 80% diesel fuel (B20) for use in most applications that use diesel fuel. You can even use it in its pure form (B100) if you take proper precautions. The word *biodiesel* in this report refers to the pure fuel—B100—that meets the specific biodiesel definition and standards approved by ASTM International. A number following the "B" indicates the percentage of biodiesel in a gallon of fuel, where the remainder of the gallon can be No. 1 or No. 2 diesel, kerosene, jet A, JP8, heating oil, or any other distillate fuel.1.

Today, B20 is the most common biodiesel blend in the United States because it balances property differences with conventional diesel, performance, emission benefits, and costs. B20 is also the minimum blend level allowed for Energy Policy Act of 1992 (EPAct) compliance. B20 can be used in equipment designed to use diesel fuel. Equipment that can use B20 includes compression-ignition (CI) engines, fuel oil and heating oil boilers, and turbines. Higher blend levels, such as B50 or B100, require special handling and fuel management and may require equipment modifications such as the use of heaters or changing seals and gaskets that come in contact with the fuel to those compatible with high blends of biodiesel. The level of special care needed largely depends on the engine and vehicle manufacturer. High blend levels are not recommended for the first-time biodiesel consumer. The ASTM standard for B100 to be used as a blend stock is D6751. Diesel fuel is defined in ASTM D975. ASTM D396 defines heating oil's. A-A-59693A defines B20 for military use.

1.3 TRIGIYCERIDE AS DIESEL FUEL

The main resources for biodiesel production can be non-edible oils obtained from plant species such as Jatropha curcas, Pongamia pinnata, Ricinus communis (caster), Cerbera odollam (sea mango).Hevea brasilliensis (rubber tree) Calaphyllum inophyllum (polanga), S. chinerisis (jojoba). Madhuca indica (mahua) and Theretia peruviana etc[3].

There are large numbers of edible and non-edible plant species for which engine test and physico-chemical laboratory test have already been conducted. In contrast to edible oil, non-edible oils like Jatropha, Castor, Karanja, Rubber seed and Sea mango are not suitable for human consumption due to the presence to toxic compounds in the oil. The seed of P. pinnata contain pongam oil which is bitter and non-edible with disagreeable taste due to the presence of flavonoid constituents, pongamin and karajin. This seed is usually used as fish poison. Plantation cost in terms of per kg oil from non-edible oil crops is lower than the plantation cost for edible oil crops with the only exception of palm oil.

The existing potential for tree borne oil seeds in India is 3.0-3.5 million tonnes, but the collection of only 0.5-0.6 million tonnes is being realized. In India, use of edible oils for biodiesel production is not practicable because of the big gap in demand and supply of edible oils[3]. Shows table 4.

Table- 4 Estimated yield of non-edible oil seeds plant

Scientific name	Plant type	Plant part	Oil yield(kg/ha
Azadirachta indica (Neem)	Tree	Seed	2670
Calophyllum inophyllum (Polanga)	Tree	Seed	4680
Hevea brasiliensis (Rubber)	Tree	Seed	40-50
Jatropha curcas (Physic nut)	Tree/ shrub	Seed	1900-2500
Pongamia pinnata	Tree	Seed	225-2250
Ricinus communis	Tree/ shrub	Seed	450
Simarouba glauca (Paradise tree)	Tree	Seed	900-1200
Thevetia peruvina (Yellow oleander)	Shurb	Seed	1575

1.3 A Composition of vegetable oils

The basic constituent of vegetable oils is triglyceride. Vegetable oils comprise 90 to 98% triglycerides and small amounts of mono- and triglycerides. Triglycerides are esters of thee fatty acids and one glycerol. These contain substantial amounts of oxygen in its structure. Fatty acids vary in their carban chain length and in the number of double bonds. The structures of common fatty acids are given Table 5 (Srivastava et al.2000; Antony et al. 2011). Table 6 summarizes the fatty acid composition of some vegetable oils (Srivastava et al 2000; Singh et al 2010; Jain S et al 2010; Kwanchareon et al 2006; and Bobade et al 2012. The fatty acids which are commonly found in vegetable oils are stearic, palmitic, oleic, linoleic and linolenic. Vegetable oils contain free fatty acids (generally 1 to 5%), phospholipids, phosphatides, carotenes, tocopherols, Sulphur compounds and traces of water.

Table- 5
Chemical structure of common fatty acids

Fatty acid	Systematic name	Structure	Formula
Lauric	Dodecanoic	12:0	$C_{12} H_{24} O_2$
Myristic	Tetradecanoic	14:0	$C_{14} H_{28} 0_2$
Palmitic	Hexadecanoic	16:0	$C1_{16} H_{32} 0_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36} 0_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40} 0_2$
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-Octadecatrienoic18	18:3	$C1_{18} H_{30} O_2$
Erucic	cis-13- Docosenoic	22:1	$C_{18}H_{42} O_2$

Table- 6
Fatty acid composition of some selected non-edible and edible oils

	14:0	16:0	18:0	20:0	22:0	24:0	18:1	18:2	18:3
Karanja	-	3.7-7.9	2.4-8.9	-	-	-	44.5-71.3	10.8-18.3	-
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	-
Mahua	-	16.0-28.2	20.0-25.1	0.0-3.3	-	-	41.0-51.0	8.9-13.7	-
Sal	-	4.5-8.6	34.2-44.8	6.3-12.2	-	-	34.2-44.8	2.7	-
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	-
Soyabean	0.0-0.09	10.83-12	3-3.61	0-0.40	-	0-0.20	23-24.9	52.74-55	6-6.04
Sanflower	0-0.07	6-6.57	3-3.44	0-0.26	-	0-0.28	17-28.59	59.50-74	0-0.08
Rapseed	0-0.6	3-4.60	1-1.77	0-0.63	-	0-0.33	62.37-64	19.32-22	8-8.3
Peanut	0-0.0	8.17-11	1.73-2	0-90-1	-	2-2.42	48-54.12	27.96-32	0.19-1
Jatropha curcas linn	0-1.4	14.1-15.6	6.8-9.7	0.2-0.4	-	0-3.6	38.6-40.8	32.1-35.0	0-0.2
Pongamia pinnata pierre	0.2-0.26	10.6-16.2	6.8-24.1	0-4.1	-	1.1-2.4	44.5-71.3	18.8-19	-
Cottonseed	0	28-28.7	0.9-1	0	0	-	13.0	57.4-58	0
Tabacco	0.09-0.17	8.87-10.96	3.34-3.49	-	-	-	12.4-14.54	67.75-69.99	0.69-4.20
Sesame	0	13-13.1	3.9-4	0	0	0	52.8-53	30-30.2	-
Palm	-	35-42.6	4.4-7	0	-	-	40.5-44	10.1-14	-
Tallow	0-2.73	22.9-23.3	19.3-19.44	o-o.14	-	-	41.60-42.4	2.9-3.91	0.9-0.49

1.4 B Fuel-related properties of vegetable oils

The fuel-related properties of vegetable oils are listed in Table 7 (Srivastava et al 2000). The kinematics viscosity of vegetable oils varies in the range of 30-40 cSt at 38° C. High viscosity of these oils is due to large molecular mass and chemical structure. Vegetable oils have high molecular weights in the range of 600 to 900, which are three or more times higher than diesel fuels. The flash points of vegetable oils are three or more times higher than diesel fuels. The flash points of vegetable oils are very high (above 200° C). The volumetric heating values of these oils are in the range of 39 to 40 MJ/kg which are low compared to diesel fuels (about 45 ml/kg). The presence of chemically bound oxygen in vegetable oils lowers their heating values by about 10%. The cetane numbers are in the range of 32 to 40. The iodine value ranges from 0 to 200 depending upon unsaturation. The cloud and pour point of vegetable oils are higher than that of diesel fuels.

Table- 7
Vegetable oil properties

Vegetable oil	Kinematic viscosity at 38 ^{0}C(mm^2/s)	Cetane No. ^{0}C	Heating value mj/kg	Cloud point ^{0}C	Pour point ^{0}C	Flash point	Density kg/l	Carbon Residue wt%
Corn	34.9	37.6	39.5	-1.1	-4.0	277	0.9095	0.24
Cottonseed	33.5	41.8	39.5	1.7	-15	234	0.9148	0.24
Cramble	53.6	44.6	40.5	10.0	-12.2	274	0.9048	0,23
Linseed	27.2	34.6	39.3	1.7	-15.0	241	0.9236	0.22
Peanut	39.6	41.8	39.8	12.8	-6.7	271	0,9026	0.24
Repeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115	0.30
Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9194	0.25
Sesame	35.5	40.2	39.3	-3.9	-9.4	260	0.9133	0.24
Soyabean	32.6	37.9	39.6	-3.9	-12.2	254	0.9138	0.25
Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161	0.27
Palm	39.6	42.0	-	31.0	-	267	0.9180	0.23
Babssu	30.3	38.0	-	20	-	150	0.9460	-
Diesel	30.6	50	43.8	-	-16	76	0.855	-

1.1 C Performance of vegetable oils as diesel fuels

It has found that use of vegetable oils as diesel fuels in conventional diesel engines leads to a number of problems which are related to the type and grade of oil and local climatic condition Rao PS et al 1991 and Ziejewski M *et al 1983*). The injection, atomization and combustion characteristics of vegetable oils in diesel engines are significantly different from those of hydrocarbons-based diesel fuels. The high viscosity of vegetable oils interferes with the injection process and leads to poor fuel atomization. The inefficient mixing of oil with air contributes to incomplete combustion. The high flash point attributes to its lower volatility characteristics. This leads to more deposit formation, carbonization of injector tips, ring sticking and lubricating oil dilution and degradation. The combination of high viscosity and low volatility of vegetable oils causes poor cold engine start up, misfire and ignition delay. Oxidative and thermal polymerizations of vegetable oils cause a deposition on the injectors forming a film that will continue to trap fuel and interfere with combustion. In the long-term operation, vegetable oil normally develops gumming, injector coking and ring sticking. Another problem is incompatibility with conventional diesel fuels. Therefore, the engine must be more or less modified according to the condition of use and the oil involved. The modified engines built by Elsbett in Germany and Malaysia and Diesel Mortenund Geraetabau GmBH (DMS) in Germany and in the USA show a good performance when fuelled with vegetable oils of different composition and grades.

1.2 DERIVATIVES OF TRIGLYCERIDES AS DIESEL FUELS

Considerable efforts have been made to develop vegetable oil derivatives that approximate the properties and performance of the hydrocarbon-based diesel fuels. The problems with substituting triglycerides for diesel fuels are mostly associated with their high viscosities, low volatilities and polyunsaturated character. These can changes in at least four ways:

1.4A Pyrolysis

Pyrolysis is strictly defined as the chemical conversion of one substance into another by means of thermal energy in absence of air with the aid of a catalyst. It involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules. The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. The pyrolyzate had lower viscosity; flash of pyrolyzate was also lower. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil. Catalytic cracking of vegetable oils to produce biofuels has been studied.

The equipment of thermal cracking and pyrolysis is expensive for modest throughputs. In addition, while the products are chemically similar to petroleum derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produced some low value materials and, sometimes, more gasoline than diesel fuel.

1.4 B Microemulsification

One of the potential solutions to the problem of the high viscosity of vegetable oils is the formation of micro emulsions with solvents such as methanol, ethanol and 1-butanol. A micro emulsion is defined as a transparent, colloidal equilibrium dispersion of optically isotropic fluid microstructures with droplet diameter generally in range100-1000 A range formed spontaneously from two normally immiscible liquids and one or more ionic or nonionic amphiphiles. A micro-emulsion can be made of vegetable oils with as ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant and a Cetane improver, with or without diesel fuels. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles. No significant deteriorations in performance were observed, but irregular injector needle sticking, heavy carbon deposits, incomplete combustion and an increase of lubricating oil Viscosity were reported.

1.4 C Dilution

Filtered, used frying oil, used cooking oil and a blend of 95% used cooking oil and 5% diesel fuel have been used directly. Blending or preheating was used as needed to compensate for cooler ambient temperatures. There were little and/or no coking and carbon buildup problems. Only problem reported was lubricating oil contamination (viscosity increase due to polymerization of polyunsaturated vegetable oils).

Two severe problems associated with the use of vegetable oils as fuels were oil deterioration and incomplete combustion. Polyunsaturated fatty acids were very susceptible to polymerization and gum formation caused by oxidation during storage or by complex oxidative and thermal polymerization at the higher temperature and pressure of combustion. The gum did not combust completely, resulting in carbon deposits and lubricating oil thickening. Dilution of vegetable oils can be accomplished with such materials as diesel fuels, solvent or ethanol. Direct use of vegetable oils/or the use of blends or the oils has generally been considered to be not satisfactory and impractical for both direct and indirect diesel engines. The high viscosity, surface tension, acid composition, free fatty acid content, as well as gum formation due to oxidation and polymerization during storage and combustion, carbon deposits and lubricating oil thickening are obvious problems.

1.4 D Transestrification (Alcoholysis)

Transesterification (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the product side. To complete a transesterification stoichiometrically, a 3:1 molar ratio of alcohol to triglycerides is needed. Transesterification can be alkali catalyzed or acid catalyzed.

1.4 E Acid Catalyzed System

This way of production is the conventional way of making the biodiesel. The idea is to use the triglycerides with alcohol and instead of a base to use an acid -the most commonly used is sulfuric acid. This type of catalyst gives very high yield in esters but the reaction is very slow, requiring almost always more than one day finishing. As in the alkali reaction, if an excess of alcohol is used in the experiment then better conversion of triglycerides is obtained, but recovering glycerol becomes more difficult and that is why optimal relation between alcohol and raw material should be determined experimentally considering each process as a new problem.

The possible operation condition is, usually, molar ratio 3:1. The type of alcohol, as well as the oils, is the same as the one that can be used in alkali catalyst reaction. The amount of catalyst supposed to be added to the reactor varies from 0.5 to 1 mol% .The temperature range varies from 55 to 60 ^{o} C. The acid transesterification is a great way to make biodiesel if the sample has relatively high free fatty acid content. In general, a 1 mol% of sulfuric acid is a good amount for a final conversion of 99% in a time around 50 hr.

1.4 F Alkali Catalyzed System

One limitation to the alkali-catalyzed process is its sensitivity to the purity of the reactants. The alkali-catalyzed system is very sensitive to both water and free fatty acid. The presence of ester may cause ester saponification under alkaline conditions. Also, free fatty acids can react with an alkali catalyst to produce soaps & water. Saponification not only consumes the alkali catalyst, but also the resulting soaps can cause the formation of emulsions. Emulsion formation creates difficulties in downstream recovery & purification of the biodiesel. Thus, dehydrated vegetable oil with less than 0.5 wt% free fatty acids, and anhydrous alkali catalyst & anhydrous alcohol are necessary for commercially viable alkali catalyzed system. This requirement is likely to be a significant limitation to the use of waste cooking oil as a low-cost feedstock. Glycerine was employed as liquid entraining agent to purify the refined oil. The process description includes a pretreatment unit, including esterification of free fatty acids, glycerine washing and methanol recovery, water washing, FAME purification, alkali removal, and glycerine purification.

1.5 **ADVANTAGES AND DISADVANTAGES OF BIODIESEL:**

1.5 A Advantages

1. Biodiesel can be produced from any fat or vegetable oil, including waste cooking oil.
2. Biodiesel can also be stored anywhere like petroleum diesel fuel and in diesel tanks and pumped with regular equipment except in colder weather, where tank heaters or agitators may be required.
3. Biodiesel is a substitute or extender for traditional petroleum diesel for which special pumps or high pressure equipment for fueling are not required. In addition, it can be used in conventional diesel engines, so there is no need to buy special vehicles or engines to run biodiesel.
4. Biodiesel also produces fewer particulate, carbon monoxide, and sulfur dioxide emissions, all targeted as public health risks by the Environmental Protection Agency. Biodiesel contains only trace amounts of sulfur, typically less than the new EPA standards that will go into effect in 2006 for diesel fuel.
5. Since biodiesel can be used in conventional diesel engines, the renewable fuel can directly replace petroleum products; reducing the country's dependence on imported oil.
6. Biodiesel offers safety benefits over petroleum diesel because it is much less combustible, with a flash point greater than 150°C, compared to 77°C for petroleum diesel. It is safe to handle, transport, and store, and has a higher flash point than petroleum diesel.
7. Biodiesel mixes readily with petroleum diesel at any blend level, making it a very flexible fuel additive.
8. Engine running on biodiesel, operate normally and have similar fuel consumption. Power output and engine torque are relatively unaffected by biodiesel.
9. Every liter of biodiesel replaces 0.95 litre of petroleum-based diesel over its life cycle. It is also very energy efficient. For every unit of fossil energy used to produce biodiesel, 3.37 units of biodiesel energy are created. Additionally, because biodiesel is nontoxic and biodegradable, it is an excellent fuel for use in fragile environments such as estuaries, lakes, rivers, and national parks.

1.5 B Disadvantages

1. Large spills of Biodiesel can harm the environment.
2. Coking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or even prevented as a result of plugged orifices.
3. Deposits on engine components (carbon, olefins, Traces of glycosides).
4. Lower energy content (5- 7 % less than distilled fuel).
5. Thickening or gelling of the lubricating oil as a result of contamination by vegetable oils- Lubricating problems
6. Engine oil degradation
7. Marginal NOx increase (1-6%)

1.5 C Emissions Reductions with Biodiesel

Since Biodiesel is made entirely from vegetable oil, it does not contain any sulfur, aromatic hydrocarbons, metals or crude oil residues. The absence of sulfur means a reduction in the formation of acid rain by sulfate emissions that generate sulfuric acid in our atmosphere. The reduced sulfur in the blend will also decrease the levels of corrosive sulfuric acid accumulation in the engine crankcase oil over time. The lack of toxic and carcinogenic aromatics (benzene, toluene and xylene) in Biodiesel means the fuel mixture combustion gases will have reduced impact on human health and the environment

Biodiesel reduces tailpipe particulate matter (PM), hydrocarbon (HC), and carbon monoxide (CO) emissions from most modern four-stroke CI engines. These benefits occur because the fuel (B100) contains 11% oxygen by weight. The presence of fuel oxygen allows the fuel to burn more completely, so fewer unburned fuel emissions result. This same phenomenon reduces air toxics, because the air toxics are associated with the unburned or partially burned HC and PM emissions. Testing has shown that PM, HC, and CO reductions are independent of the feedstock used to make biodiesel. The EPA reviewed 80 biodiesel emission tests on CI engines and has concluded that the benefits are real and predictable over a wide range of biodiesel blends. In older two-stroke engines, B20 can reduce CO, HC, and PM if the engines do not consume excessive amounts of lube oil. If lube oil consumption is high, PM benefits from B20 use may be less. In addition, one of the first benefits that people notice when using biodiesel or biodiesel blends is the smell. Using biodiesel can make diesel exhaust smell better; more like cooking odors.

1.5 D Lower Hydrocarbon Emissions

Biodiesel is comprised of vegetable oil methyl esters, that is, they are hydrocarbon chains of the original vegetable oil that have been chemically split off from the naturally occurring triglycerides. Biodiesel hydrocarbon chains are generally 16 to 20 carbons in length and they are all oxygenated at one end making the product an excellent fuel. Several chemical properties of the Biodiesel allow it to burn cleanly and actually improve the combustion of petroleum diesel in blends. As a result of cleaner emissions, there will be reduced air and water pollution from boats operated on Biodiesel blends.

1.5 E Carbon Monoxide Emissions

Carbon monoxide gas is a toxic byproduct of all hydrocarbon combustion that is also reduced by increasing the oxygen content of the fuel. More complete oxidation of the fuel results in more complete combustion to carbon dioxide rather than leading to the formation of carbon monoxide.

1.5 F Biodiesel Helps Reduce Greenhouse Gases

Unlike other clean fuels such as compressed natural gas (CNG), Biodiesel and other biofuels are produced from renewable agricultural crops that assimilate carbon dioxide from the atmosphere to become plants and vegetable oil. The carbon dioxide released this year from burning vegetable oil biodiesel, in effect, will be recaptured next year by crops growing in fields to produce more vegetable oil starting material. Fossil fuel combustion accounts for 70% of the total anthropogenic CO_2 contribution. Supplementing our dwindling fossil fuel reserves with biomass-based fuels (Biodiesel, for petrodiesel; biomass-based alcohols or hydrogen for gasoline) helps reduce the accumulation of $CO_{2.}$

1.5 G Lower Impact on Marine Environment

Water pollution should also be reduced by using biodiesel in boat engines since there will be more efficient burning of the fuel mixture, less carbon (soot) accumulation and particulate (smoke) emissions. Faster starting and smoother operation also should reduce the discharge of unburned fuel. Any accidental discharges of small amounts of Biodiesel should have relatively little impact on the environment compared to petroleum diesel, which contains more toxic and more water-soluble aromatics. Nonetheless, the methyl esters could still cause harm. Environment because biodiesel is a simple, straight carbon chain with two oxygen at one end (mono-alkyl ester), it is more readily metabolized by bacteria that normally break down fats and oils in the environment. The petroleum diesel hydrocarbons lack oxygen, and represent a very complex mixture of hydrocarbons with multiple double bonds, and many other branched, cyclic and cross linked chains. The more complex chemical structures of diesel hydrocarbons make them more difficult to biodegrade, and in many cases, toxic.

1.5 H Properties of biodiesel

The properties of biodiesel and diesel fuels are compared in Table 8 Dunn R.O *et al 1995;* Dunn R.O et al 2002 and *Dunn* R.O *et al 1996).* The characteristics of biodiesel are close to diesel fuels, and therefore biodiesel becomes a strong candidate to replace the diesel fuels if the need arises. The conversion of triglycerides into methyl or ethyl esters through the transestrification process reduces the molecular weight to one-third that of the triglyceride reduces the viscosity by a factor of about eight and increases the volatility marginally. Biodiesel has viscosity close to diesel fuels. These esters contain 10 to 11% oxygen by weight, which may encourage more combustion than hydrocarbon-based diesel fuels in an engine. The cetane number of biodiesel is around 50. The use of tertiary fatty amines and amides can be effective in enhancing the ignition quality of the finished diesel fuel without having any negative effect on its cold flow properties. Since the volatility increases marginally, the starting problem persists in cold conditions. Biodiesel has lower volumetric heating values (about 12%) than diesel fuels but has a high cetane number and flash point. The esters have cloud point and pour point that are 15 to 25^0 C higher than those of diesel fuels.

Table- 8
Properties of Biodiesel

Biodiesel	Cloud point ^{0}C	Pour point ^{0}C	Cold-filter plugging point ^{0}C	Kinematic viscosity mm^2/s	Cetane no.	Lower heating value mj/kg	Flash point	Density kg/l	Refer ences
Rapeseed	-3	-9	-14	-	-	-	-	-	15
Sunflower	4	-6	-7	4.6	49	33.5	183	0.860	7
Soybean	2	0	-4	4.5	45	33.5	178	0.885	7
Peanut	20	15	17	4.9	54	33.6	176	0.883	7
Palm	12	12	9	5.7	62	33.5	164	0.880	7
Babassu	4	-	-	3.6(37.8^{0}C)	54	33.6	176	0.883	2

Tallow	12	9	-	-	-	-	96	-	2
Rapeseed b	-	-	-	4.2 (40.0 ^{0}C)	51-59.7	32.8	-	0.882	2
Palm b	-	-	-	4.3-4.5 (40 ^{0}C)	64.3-70	32.4	-	0.872-0.877	2
Soybean b	-	-	-	4.0(40 ^{0}C)	45.7-56	32.7	-	0.880	2
Diesel	-	-16	-	3.06	50	43.8	76	0.855	2
20% BD blend	-	-16	-	3.2	51	43.2	128	0.859	2

6. Conclusion

India has rich and abundant forest resources with a wide range of plants and oilseeds. The production of these oilseeds can be stepped up many folds if the government takes the decision to use them for producing diesel fuels. Non-edible oils such as jatropha, rice bran, neem, mahua, karanja, babassu, etc. are easily available in many parts of the world including India, and are cheap compared to edible oils. Jatropha whose seeds are rich in oil is a hardy plant that can grow in near absence of water. Jatropha plants have a productive life of up to 40 years, but take 2 to 3 years to mature. The yield of oil could be as high as 3000 kg/hectare. The cost of biodiesel depends upon two factors-the cost of seeds used in oil extraction and the cost of processing of raw oil. The cost of processing of raw oil is reported to be Rs. 3 to 4 per kg. The economic feasibility therefore depends on availability of oil at a reasonable price. However, since jatropha has no commercial use, there is no cultivation as of now, and availability of seeds for oil production is a problem. However, a number of plants are believed to be coming up in Rajasthan and Haryana. Indian Railways has signed an MOU with IOC for a 500 hectare jatropha plantation.

It is proposed to study the extraction of jatropha oil from seeds and subsequently prepare biodiesel from jatropha oil. The proposed use of jatropha oil for making biodiesel is likely to be technically acceptable, economically competitive, environmentally acceptable and easily available in near future as Indian government has decided to enhance the production of jatropha seeds. The proposed study of the extraction of oil from Jatropha seeds using hydrocarbon solvents is likely to generate the required data on solid-liquid equilibria at several temperatures to design large continuous extraction plants. The process of making biodiesel from jatropha oil is to be developed at the laboratory scale and the process variables such as ratio of alcohol to oil, reaction temperature, catalyst type and concentration and mixing intensity are to be optimized. The data generated in this study are needed for the design of continuous plants for the manufacture of biodiesel from triglycerides such as jatropha oil. Kinetics of transesterification reaction will be studied to provide the required data for the design of transesterification reactors. Biodiesel production and further investigation of physical and chemical properties of biodiesel.

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