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Review Article

Prospects of using vegetables, *Jatropha curcas* and Algae oils for Biodiesel production

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Abstract

Biodiesel is a biodegradable, nontoxic alternative fuel with properties similar to conventional diesel. It is prepared from renewable resources i.e. vegetable oils and animal fats. The use of vegetable oils such as palm, soybean, sunflower, peanut and olive oil etc as alternative fuels for diesel engines dates back almost nine decades. Vegetable oils have attracted as an alternative energy source. The most detrimental properties of vegetable oils are its high viscosity and low volatility, and these cause several problems during their long duration usage in compression ignition engines. The most commonly used methods to make vegetable oil suitable for use in compression ignition is to convert it into biodiesel i.e. oil esters using process of transesterification.

Key words: Biodiesel, vegetable oils, transesterification, waste cooking oil.

Introduction

Biodiesel has gained importance in the recent part for its ability to replace fossil fuels which are likely to run out within a century. The environmental issues concerned with the exhaust gases emmission by the usage of fossil fuels also encourage the use of biodiesel which has proved to be ecofriendly far more than fossil fuels (Peterson and Auld, 1996). Biodiesel is a mixture of mono-alkyl esters obtained from vegetables like soybean, Jatropha, rapeseed, palm, sunflower, corn. peanut, canola and cotton seed oil etc (Barnwal and Sharma, 2005). Apart from vegetables, biodiesel can also be produced from other sources like animal fat, waste cooking oil, greases (trop grease, float grease) and algae **(**Feugo and Gros, 1949**)**.Biodiesel is gaining more and more importance as an attractive fuel due to the depleting fossil fuel resources. Chemically biodiesel is mono-alkyl eaters of long chain fatty acids derived from renewable feed stock like vegetable oils and animal fats. It is produced by transesterification in which oil or fat is reacted with a monohydric alcohol in presence of a catalyst (Meher *et al*., 2006). Due to increase in the petroleum and the environmental concerns about pollution coming from the car gases, Biodiesel is becoming a developing area of high concern. There are different ways of production, with different kind of raw materials: refine, crude, or frying oils.

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One of the advantages of this fuel is that the raw material used to produce it is natural and renewable. All these type of oils came from vegetable or animal fat, making it biodegradable and nontoxic (Ma and Hanna, 1999).

Vegetable oil as a Biodiesel source

Vegetable oils bearing, renewable, are widely available from a variety of sources and have low sulpher contents close to zero, and hence called less environmental damage (lower green house effect) than diesel. Vegetable oils such as palm, soybean, sunflower, peanut, and olive oil are used as alternative fuel for diesel engines. Depending upon the climate and the soil condition, different countries are looking for different types of vegetable oils as substitutes for diesel fuels. For example, soybean oil in the U.S, rapeseed and sunflower oils in Europe, palm oil in south East Asia, and coconut oils in the Philippines are being considered (Goering et al., 1982).

Characteristics of oils affecting their suitability for use as fuel

Calorific Value, Heat of Combustion

Heating Value or Heat of Combustion is the amount of heating energy released by the combustion of a unit value of fuels. One of the most important determinants of heating value is moisture contents. Air-dried biomass typically has about 15-20% moisture, whereas the moisture content for oven-dried biomass is negligible. Moisture content in coals varies in the range 2-30%. However, the bulk density (and hence energy density) of most biomass feed stocks is generally low, even after densification – between about 10 and 40% of the bulk density of most fossil fuels. Liquid biofuels however have bulk densities comparable to those for fossil fuels.

Melt Point or Pour Point

Melt or pour point refers to the temperature at which the oil in solid form starts to melt or pour. In cases where the temperatures fall below the melt point, the entire fuel system including all fuel lines and fuel tank will need to be heated.

Cloud Point

The temperature at which oil starts to solidify is known as the cloud point. While operating an engine at temperatures below oil's cloud point, heating will be necessary in order to avoid waxing of the fuel.

Flash Point (FP)

The flash point temperature of diesel fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source. Flash point varies inversely with the fuel's volatility. Minimum flash point temperatures are required for proper safety and handling of diesel fuel.

Iodine Value (IV)

Iodine Value (IV) is a value of the amount of iodine, measured in grams, absorbed by 100 grams of given oil. Iodine value (or Iodine number) is commonly used as a measure of the chemical stability properties of different biodiesel fuels against such oxidation as described above. The Iodine value is determined by measuring the number of double bonds in the mixture of fatty acid chains in the fuel by introducing iodine into 100 grams of the sample under test and measuring how many grams of that iodine are absorbed. Iodine absorption occurs at double bond positions - thus a higher IV number indicates a higher quantity of double bonds in the sample, greater potential to polymerize and hence lesser stability.

Iodine Numbers for some plant oils (before conversion into biodiesel):

Coconut oil	:	10
Rapeseed oil	:	94-120
Soybean oil	:	117-143
Sardine oil	:	185

Iodine Numbers after conversion to biodiesel through transesterification (approximate values):

Rapeseed Methyl Ester (Rapeseed Biodiesel)	:	97
Rapeseed Ethyl Ester	:	100
Soy Ethyl Ester (Soy biodiesel variety1):		123
Soy Methyl Ester (Soy biodiesel variety2):		133

Viscosity

Viscosity refers to the thickness of the oil, and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size. Viscosity affects injector lubrication and fuel atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection, which can cause poor combustion, increased exhaust smoke and emissions.

Aniline Point/Cetane Number (CN)

Cetane Number is a relative measure of the interval between the beginning of injection and auto ignition of the fuel. The higher the cetane number, the shorter the delay interval and the greater its combustibility. Fuels with low cetane Numbers will result in difficult starting, noise and exhaust smoke. In general, diesels engines will operate better on fuels with Cetane numbers above 50.Cetane tests provide information on the ignition quality of a diesel fuel. Research using cetane tests will provide information on potential tailoring of vegetable oil-derived compounds and additives to enhance their fuel properties.

Density

Density is the weight per unit volume. Oils that are denser contain more energy. For example, petrol and diesel fuels give comparable energy by weight, but diesel is denser and hence gives more energy per litre (Muniyappa *et al*., 1996).

The aspects listed above are the key aspects that determine the efficiency of a fuel for diesel engines. There are other aspects characteristics, which do not have a direct bearing on the performance, but are important for reasons such as environmental impact etc. These are:

Ash Percentage

Ash is a measure of the amount of metals contained in the fuel. High and injection system wear. Ash content for bio-fuels is typically lower than for most coals, and sulpher content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a soil amendment to help replenish nutrients removed by harvest.

Sulfur Percentage

The percentage by weight, of sulfur in the fuel Sulfur content is limited by low to very small percentages for diesel fuel used in on-road applications. The fuel properties of vegetable oils have also been shown in table-1 that indicates the kinematics viscosity of vegetable oils varies in the range of 30-40^{o}C at 38^{o}C. The high viscosity of these oils is due to their molecular mass in the range of 60^{0}-90^{0}, which is about 20 times higher than Diesel fuel. The flash point of vegetable oils is very high (above 200^{o}C). The volumetric Heating values are in the range of 39-40 MJ/Kg, as compared to diesel fuel (about 45MJ/Kg). The cetane no is in the range of 32-40 (Mittelbach and Remschmidt, 2004).

Chemical composition of Vegetable oils

Vegetable oils also known, as triglycerides comprise of 98% triglycerides and small amount of mono and diglycerides. Triglycerides are esters of three molecules of fatty acids and one glycerol and certain substantial amounts of oxygen in the number of double bonds. Different types of oils have different types of fatty acids (Marckley, 1960). The formula and structures of various fatty acids present in vegetable oils are given in the table-2.

Waste vegetable oil (Refinery waste) as a Biodiesel source

Acid oil, which is a by-product in vegetable oil refining, mainly contains free fatty acids (FFAs) and acylglycerols, and is a candidate of material for Biodiesel fuel. In order to provide FAMEs at a reasonable price, production of FAMEs not only from refined vegetable oils, but also from crude or waste material and from by-products of oil processing has been attempted; one of the materials is acid oil. Alkali deacidification, one of the steps in vegetable oil refining, by-produces soap stock that mainly contains soap and water. Acid oil is obtained by acidulation of the soap stock, and contains free fatty acids (FFAs), acylglycerols, and other lipophylic compounds; It is reproduced currently as industrial FFAs, although their demand is almost in saturation. Conversion of the acid oil to Biodiesel fuel is thus expected to avoid oversupply of the industrial FFAs and their price down. A mixture (Acid oil model) or refined FFAs was recently reported to be converted to fatty acid methyl esters (FAMEs) at >98% conversion by two step reaction system comprising methyl esterification of FFAs and methanolysis acylglycerols using immobilized *Candida antarctica* lipase (Mudge and Pereira, 1999; Hass *et al*., 2003; Yomi *et al*., 2007).

Jatropha curcas as a Biodiesel Source

Jatropha curcus, belonging to the family Euphorbiaceae, is a low-growing tree, native to South America, but widely cultivated also throughout Central America, Africa and Asia. *Jatropha*, which is not eaten by animals, is a vigorous, drought and pest-resistant plant that is planted in tropical countries principally as a hedge, protecting cropland freely ranging cattle, sheep and goats. The popularity of *Jatropha* is also based on the use of its oil and other derivatives, although limited, for medicinal purposes and the manufacture of soap. *Jatropha* is unique renewable energy sources in terms of the number of potential benefits that can be expected to result from its widespread cultivation. Its cultivation requires simple technology. The seed yield for *Jatropha* varies from 0.5 to 12 tons /year/ha-depending on the soil, nutrient and rainfall conditions- and the trees have a protective life of over 30 years. An average annual seed production of about five tons/ha can be expected on good soil when rainfall is 900-1,200mm.The seeds contain about 30% oil that can be converted into biodiesel by a process called Transesterification, in which a simple alcohol (e.g. methanol) replaces glycerol from the vegetable oil molecules (these are triglycerides, i.e.; three molecules of fatty acid molecules are attached to a glycerol molecule). The suitability of *Jatropha* seed oil for transesterification into biodiesel has also been clearly demonstrated. *Jatropha* oil contains about 14% free fatty acids, which are for beyond the limit of 1% FFA level that can be converted into Biodiesel by transesterification using alkaline catalyst (Tiwari *et al*., 2007) (Table-3)

Chemical Constituents of the *Jatropha curcas* plant

Five diterpenes were isolated from the roots of Jatropha *cur*cas (Narasimharao *et al*., 2007). Six unstable intermolecular diterpene esters were isolated from the seed oil of *Jatropha curcas*. Five of these, *Jatropha* factors C (2)-C (6) (3-7), are new natural products, and the structure of the known *Jatropha* factor C (1) (2) has been revised. All compounds possess the same diterpene moiety, namely, 12-deoxy-16-hydroxyphorbol. The dicarboxylic acid moieties of 2-5 contain a bicyclo hexane unit and those of 6 and 7 a cyclobutane unit, which is described for the first time within this compound class. Compounds 4 and 5 are C-8' epimers. The structures of 2-7 were elucidated by spectroscopic methods and give an insight into the biogenesis of the characterized substances (Hass *et al*., 2003). Ravindranath and coworkers isolated twenty constituents, among whom four diterpenoids were unknown and six compounds, tetradecyl- (E)-ferulate, 3-O-(Z)-coumaroyl oleanolic acid, heudelotinone, epi-sojatrogrossidione, 2alpha-hydroxy-epi-sojatrogrossidione, and 2-methyanthraquinone had not been reported earlier from this species (Laforgia and Ardito, 1994).

Biodiesel from Algae: Oilgae – Oil

While a number of bio-feedstock are currently being experimented for biodiesel (and ethanol) production, algae have emerged as one of the most promising sources especially for biodiesel production, for two main reasons (1) The yields of oil from algae are orders of magnitude higher than those for traditional oilseeds, and (2) Algae can grow in places away from the farmlands & forests, thus minimising the damages caused to the eco- and food chain systems. There is a third interesting reason as well: Algae can be grown in sewages and next to power-plant smokestacks where they digest the pollutants and give us oil. Though research into algae oil as a source for biodiesel is not new, the current oil crises and fast depleting fossil oil reserves have made it more imperative for organizations and countries to invest more time and efforts into research on suitable renewable feedstock such as algae. Just by way of history, petroleum is widely believed to have had its origins in kerogen, which is easily converted to an oily substance under conditions of high pressure and temperature. Kerogen is formed from algae, biodegraded organic compounds, plankton, bacteria, plant material, etc., by biochemical and/or chemical reactions such as diagenesis and catagenesis. Several studies have been conducted to simulate petroleum formation by pyrolysis. On the basis of these findings, it can be inferred that algae grown in CO_2 enriched air can yield oil that can be converted into biodiesel. Such an approach can contribute to solving two major problems: air pollution resulting from CO_2 evolution, and future crises due to a shortage of energy sources (Gerpan, 2006).

Microbial oils, otherwise referred to as single cell oils (SCO) produced by various microorganisms, are now believed as a potential feedstock for biodiesel production due to their specific characteristics such as they are not affected neither by seasons nor by climates, they own high lipid content, can be produced from a wide variety of sources with short period of production especially from the residues with abundant nutrition, and so on (Komaitis and Aggelis, 2004). The microbial oils, however, are mainly used as commercial sources of arachidonic acid (ARA) and docosahexaenoic acid (DHA) (Eroshin *et al.*, 2010). The research on microbial oils was focused on these polyunsaturated fatty acids (PUFAs) and related report that whether it could be used for biodiesel production was few. In addition, microbial oils must be absolutely safe if used as dietary supplements while microbial oils needed not when used for biodiesel production.

Conclusion

Today's transportation services in industrialized countries are primarily based on fossil fuels especially crude oil derivatives. The spread of this fossil energy intensive approach to developing countries and economics in transitions with large populations may be constrained by limited resources availability and concerns about environment and human health. Biodiesel is becoming a developing area of high concern as a substitute for diesel fuel due to several advantaged like it can reduce our dependence on foreign petroleum, greenhouse gas emissions, air pollution and related public health risks and can benefit our domestic economy. The advantages of Biodiesel as diesel fuel are also liquid nature portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content.This review paper attempt to optimize different oil sources for the production of Biodiesel.

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Table-1 Properties of some vegetable oils as fuel.

S.No	**Vegetable oil**	**Viscosity at 38 °C (mm^2/s)**	**Cetane no °C**	**Heating value (MJ/Kg)**	**Cloud point °C**	**Pour point °C**	**Flash point °C**	**Density Kg/l**
1	Cotton	34.9	37.6	39.5	-1.1	-40	277	0.9095
2	Cottonseed	33.5	41.8	39.5	1.7	-15	254	0.9148
3	Crambe	53.6	44.6	40.5	10	-12.2	274	0.9048
4	Linseed	27.2	34.6	39.3	1.7	-15.0	241	0.9236
5	Peanut	39.6	41.8	39.8	12.8	-6.7	271	0.9026
6	Rapeseed	37.0	37.6	39.7	-3.9	-31.7	246	0.9115
7	Safflower	31.3	41.3	39.5	18.3	-6.7	260	0.9144
8	Seasome	35.5	40.2	39.3	-3.9	-9.4	260	0.9138
9	Soybean	32.6	37.9	39.6	-3.9	-12.2	254	0.9133
10	Sunflower	33.9	37.1	39.6	7.2	-15.0	274	0.9161
11	Palm	39.6	42.0	-	31.0	-	267	0.9180
12	Diesel	3.06	50	43.8	-	-16	76	0.855

Table-2 Chemical structure of common fatty acids.

S.No	**Name of fatty acids**	Structures	**Formula**
1	Lauric	12:0	$C_{12}H_{24}O_2$
2	Myristic	14:0	$C_{14}H_{28}O_2$
3	**Palmitic**	16:0	$C_{16}H_{32}O_2$
4	**Stearic**	18:0	$C_{18}H36O_2$
5	Arachidic	20:0	$C_{20}H_{40}O2$
6	Behenic	22:0	$C_{22}H_{44}O_2$
7	Oleic	18:1	$\mathbf{C_{18}H_{34}O_2}$
8	Linoleic	18:2	$C_{18}H_{32}O_2$
9	Linolenic	18:2	$C_{18}\ H_{3o}\ O_2$
10	Erucle	22:1	$C_{32}H_{42}O_2$

Table-3 Fuel properties of *Jatropha curcas*, *Jatropha* Biodiesel and Diesel.

S.No	**Property**	**Unit**	***Jatropha curcas* oil**	***Jatropha* Biodiesel**	**Diesel**
1	Density	Kgm^{-3}	940	880	850
2	Viscosity	mm^2S^{-1}	24.5	4.80	2.60
3	Flash point	°C	225	135	68
4	Pour point	°C	4	2	-20
5	Water content	%	1.4	0.025	0.02
6	Ash content	%	0.8	0.012	0.01
7	Carbon residue	%	1	0.2	0.17
8	Acid value	$MgKOH^{g-1}$	28	0.4	-
9	Calorific value	$MJKg^{-1}$	38.65	39.23	42