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Review Paper

Non-Conventional Seed Oils as Potential Feedstocks for Future Biodiesel Industries: A Brief Review

Basumatary Sanjay
Department of Chemistry, Bineswar Brahma Engineering College, Kokrajhar-783 370, Assam, INDIA

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Abstract

Due to rapid development, the worldwide demand for biodiesel as an alternative to the conventional transport fuel, petrodiesel for diesel engines, is increasing because of the limited reserves of fossil fuels, increasing prices of crude oils and environmental concerns. The use of edible vegetable oils for biodiesel production is not feasible as the demand for edible vegetable oils is tremendously increasing. Prime importance is given to alternative biodiesel feedstocks like non-conventional seed oils as these oils will not cause food crisis leading to economic imbalance. In this review paper, an attempt is being taken to identify non-conventional oils with their oil contents for future biodiesel industries.

Keywords: Non-conventional oils, feedstocks, transesterification, biodiesel.

Introduction

The conventional sources of energy such as petroleum-derived fuels, coal and natural gas are depleting and will be exhausted in the near future. The worldwide energy consumption is increasing due to rapid population growth and economic development. Because of the limited reserves of fossil fuels, increasing prices of crude oils and environmental concerns, biodiesel is a viable alternative to the conventional transport fuel, petrodiesel for diesel engines[1,2]. Biodiesel is receiving more and more attention recently because it is renewable, biodegradable, non-toxic and environment-friendly[3,4].

Biodiesel, mixture of fatty acid methyl esters (FAME), is generally produced from a varied range of edible and non-edible vegetable oils, animal fats, used frying oils and waste cooking oils by transesterification with methanol in presence of a catalyst (acid, base or biocatalyst)[5-7]. The biodiesel is quite similar to conventional diesel fuel in its physical characteristics and can be used alone or mixed in any ratio with petroleum based diesel fuel in most existing modern four-stroke combustion ignition diesel engines with very few technical adjustments or no modification. Biodiesel as a neat can be used as a direct substitute for petrodiesel and is technically called B100. The preferred ratio of mixture ranges between 5% (B5) and 20% (B20). The blending ratio has been investigated by various authors on CI engines. Up to 20% blending of biodiesel with diesel has shown no problems in engine parts[8-10].

Currently, more than 95% of the biodiesel is made from edible oils or conventional sources (soybean, rapeseed, sunflower, palm *etc.*). Continuous and large-scale production of biodiesel from edible oils may cause negative impact to the world such as depletion of food supply leading to economic imbalance[11, 12]. Taking these factors into consideration, non-conventional and non-edible oils definitely have the advantage over edible oils as biodiesel feedstocks. Therefore, exploring alternative biodiesel feedstocks like non-edible vegetable oils should be an important objective for biodiesel industries in near future.

Table-1
Common fatty acids found in vegetable oil and animal fats

Fatty acids	Number of carbons and double bonds
Capric (decanoic) acid	C 10:0
Lauric (dodecanoic) acid	C 12:0
Myristic (tetradecanoic) acid	C 14:0
Palmitic (hexadecanoic) acid	C 16:0
Palmitoleic (*cis*-9-hexadecenoic) acid	C 16:1
Stearic (octadecanoic) acid	C 18:0
Oleic (*cis*-9-octadecenoic) acid	C 18:1
Linoleic (9,12-octadecadienoic) acid	C 18:2
Linolenic (9,12,15-octadecatrienoic) acid	C 18:3
Arachidic (eicosanoic) acid	C 20:0
Gondoic (*cis*-11-eicosenoic) acid	C 20:1
Gadoleic (*cis*-9-eicosenoic) acid	C 20:1
Arachidonic (5,8,11,14-eicosatetraenoic) acid	C 20:4
Behenic (docosanoic) acid	C 22:0
Eurcic (*cis*-13-docosenoic) acid	C 22:1
Lignoceric (tetracosanoic) acid	C 24:0
Nervonic (*cis*-15-tetracosenoic) acid	C 24:1
Cerotic acid (hexacosanoic) acid	C 26:0

Feedstocks for Biodiesel Production

Biodiesel is mono alkyl esters of long chain fatty acids derived from a varied range of edible and non-edible vegetable oils, animal fats, used frying oils and waste cooking oils which have characteristics similar to petroleum-derived diesel fuel. The source for biodiesel production is chosen according to the availability in each region or country, physico-chemical properties, production cost and transportation. Any fatty acid source may be used to prepare biodiesel, but most research articles have reported soybean as a biodiesel source[11]. The common fatty acids found in vegetable oils and animal fats are shown in table-1. Generally, the most abundant vegetable oil in a particular region is the most common feedstock. Thus, soybean oil is the largest source of vegetable oil in the United States, while rapeseed (canola) and sunflower oils are the largest source in Europe. Similarly, palm oil in Southeast Asia (mainly Malaysia and Indonesia) and coconut oil in the Philippines are the largest source of vegetable oil[13-15]. Researchers have investigated for cheaper and economically viable non-edible oils as alternative feedstocks for use in biodiesel production and various biodiesel sources studied from less common or non-conventional oils are shown in table-2.

Table-2
Reported non-conventional seed oils with their oil contents

Name	Oil content (wt.%)
Yellow oleander[1]	63
Pongamia glabra[16]	33
Jatropha curcas[17,18]	30-50
Rubber (*Hevea brasiliensis*)[19]	40-50
Rocket (*Eruca sativa* Mill.)[20]	34
Terminalia belerica Robx.[21]	43
Zanthoxylum bungeanum Maxim[22]	24-28
Field pennycress[23]	29
Croton megalocarpus[14]	32
Moringa oleifera[13]	35
Coriander (*Coriandrum sativum* L.)[24]	26-29
Hemp (*Cannabis sativa* L.)[25]	26-38
Stillingia (*Sapium sebiferum* Roxb)[26]	32
Guindilla (*Guindilia trinervis*)[27]	28-29
Pistacia chinensis[28]	40
Roselle (*Hibiscus sabdariffa* L.)[29]	18
Hazelnut oil[30]	60
Calophyllum inophyllum L.[31]	75
Syagrus coronata (Mart.) Becc.[32]	39
Osage orange (*Maclura pomifera*)[33]	32
Camelina (*Camelina sativa* L.)[34]	30
Perah (*Elateriospermum tapos*)[35]	38
Schizochytrium limacinum[36]	50
Babassu (*Orbignya phalerata*)[37]	66
Gmelina arborea[3]	53
Pithecellobium monadelphum[6]	10
Mahua (*Madhuca Indica*)[38]	30-40
Neem (*Mellia azadirachta*)[38]	33-45
Simarouba glauca[7]	55-65
Soapnut (*Sapindus mukorossi*)[39]	51

Properties of Biodiesel Fuels

Since biodiesel is produced from vegetable oils of varying origin and quality, the pure biodiesel must meet before being used as a pure fuel or being blended with conventional diesel fuels. Various parameters (table-3) define the quality of biodiesel which discussed below.

Kinematic viscosity is one of the most important properties as it measures the resistance to flow due to internal friction. High values of kinematic viscosity give rise to poor fuel atomization, incomplete combustion, and carbon deposition on the injectors. Therefore, the biodiesel viscosity must be low[40]. Biodiesel fuel blends generally have improved lubricity; however, their higher viscosity levels tend to form larger droplets on injection which, can cause poor combustion and increased exhaust smoke. The viscosity of fatty acid methyl esters can go to very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, biodiesel viscosity must be nearly same to that of the diesel fuel.

Flash point of a fuel indicates the minimum temperature at which the fuel will ignite (flash) on application of an ignition source under specified conditions. Flash point varies inversely with the fuel's volatility. Flash point minimum temperatures are required for proper safety and handling of fuels[41]. It is noted that the biodiesel component must meet a flash point criteria, prior to blending, for the purpose of assuring that the biodiesel component does not contain methanol. The flash point of biodiesel is higher than the petrodiesel, which is safe for transport purpose. High values of flash point decreases the risk of fire.

Cold filter plugging point (CFPP) of a fuel reflects its cold weather performance. At low operating temperature, fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. CFPP defines the fuels limit of filterability, having a better correlation than cloud point for biodiesel as well as petrodiesel[26,41]. Normally either pour point or CFFP are specified. The cloud point of any petroleum fuel is defined as the temperature at which a cloud of wax crystals first appears in the oil when it is cooled at a specific rate. The pour point is the lowest temperature at which the oil specimen will flow. Both parameters are often used to specify cold temperature usability of fuel oils[26]. The cloud and pour points are related to the cold start of the motor. Both points must be sufficiently low, because if the biodiesel is frozen, the motor will not start.

The cetane number is a prime indicator of fuel ignition quality in the realm of diesel engines. It is conceptually similar to the octane number used for gasoline. Generally, a compound that has a high octane number tends to have a low cetane number and vice versa. The cetane number measures how easily ignition occurs and the smoothness of combustion. Higher is the cetane number better it is in its ignition properties[41]. Cetane number affects a number of engine performance parameters like combustion, stability, driveability, white smoke, noise and emissions of CO and hydrocarbons[27]. Biodiesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency.

Acid number is a measure of acids in the fuel. These acids emanate from two sources: i. acids utilized in the production of the biodiesel that are not completely removed in the production process; and ii. degradation by oxidation. For biodiesel blends the acid number will change as a result of the normal oxidation process over time. Once purchased, biodiesel fuel blends that will not be utilized immediately should be monitored for changes in acid number as an indicator of fuel degradation. A high acid value will damage fuel pumps and fuel filters[27,41].

Table-3
ASTM D6751 and EN 14214 Biodiesel (B100) Specifications

Property	ASTM D6751	EN 14214
Density (15 ^oC, g/cm^3)	NS	0.86-0.90
Kinematic viscosity (40 ^oC, mm^2/s)	1.9-6.0	3.5-5.0
Cetane number	47 (min)	51 (min)
Pour point (^oC)	NS	NS
Flash point (^oC)	130 (min)	120 (min)
Cloud point (^oC)	To report	NS
Cold filter plugging point (^oC)	NS	NS
Lubricity (60 ^oC, µm)	NS	NS
Ramsbottom carbon residue (mass %)	NS	NS
Acid value (mg of KOH/g)	0.50 (max)	0.50 (max)
Iodine value (g I_2 /100 g)	NS	120 (max)
Total sulfur (ppm)	15 (max)	10 (max)
NS: not specified. min: minimum. max: maximum		

The iodine value is related to the chemical structure of the fuel. The iodine value is a measure of the unsaturation in fats and oils. Higher iodine value indicates higher unsaturation in fats and oils[41,42]. Standard iodine value for biodiesel is 120 for Europe's EN 14214 specification. This requirement is limited by the standard limits of linolenic acid methyl ester composition for biodiesel. The limitation of unsaturated fatty acids is necessary due to the fact that heating higher unsaturated fatty acids results in polymerization of glycerides. This can lead to the formation of deposits or deterioration of the lubricating property. Fuels with this characteristic are also likely to produce thick sludges in the sump of the engine, when fuel seeps down the sides of the cylinder into the crankcase[43].

Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel. Conradsons carbon residue for biodiesel is more important than that in diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities[42,44].

Lubricity is a measure of the fuel's ability to provide adequate lubrication of the components of the fuel system, including fuel pumps and injectors[41,42]. The precision required in the manufacturing of these components and the significant influence of abnormal wear require that they be adequately protected from scuffing, scratching, wearing, etc. that may affect their fuel delivery characteristics. The level specified is consistent with that recommended by suppliers of fuel injection equipment for modern diesel engines.

One of the main criteria for the quality of biodiesel is the storage stability. From the time of production, biodiesel fuels are unstable due to the natural oxidation process[41,45,46]. The process involves a free radical chain reaction that continues until the reactive molecular links or available oxygens are depleted. Peroxides (hydroperoxides) are reactive oxidizing agents formed during the first steps of fuel oxidation. At high concentration, peroxides or the free radicals formed can damage or degrade certain plastics and elastomers, particularly at higher temperatures. Subsequent steps in the oxidation process produce acids, gums, polymers, and other insolubles. Polymers and other insoluble materials that are formed during oxidation result in fuel filter blockage[42,43]. Fuel that meets the specified limit at the time of retail sale is expected to provide six months of storage capability, depending on storage conditions, before degradation occurs. Fuel should be monitored to determine if degradation has taken place and necessary steps taken to avoid the use of degraded fuel. It is important to note that the test method utilized must be modified to use glass fibre filters to prevent degradation of the filter media by the biodiesel. If too high unsaturation results in an oxidation problem, a stabilizer (antioxidant) can be added to extend the storage life of the biodiesel.

The properties of biodiesel and diesel fuels show many similarities, and therefore, biodiesel is rated as a strong candidate as an alternative to diesel[26,41]. This is due to the fact that the conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one-third, reduces the viscosity by about one-eighth, and increases the volatility marginally. Biodiesel contains 10-11% oxygen (w/w), thereby enhancing the combustion process in an engine[43].

The presence of high level of alcohol in biodiesel cause accelerated deterioration of natural rubber seals and gaskets. Therefore control of alcohol content is required[41,44]. Biodiesel fuel mainly consists of fatty acid alkyl esters and its quantities are specified according to the specifications of various countries. The presence of mono- di- and triglycerides cause engine problems like fuel filter plugging affecting the fuel properties and are specified in most of the biodiesel standards.

Conclusion

A major challenge for economic viability of biodiesel industries is the high cost of edible vegetable oils which is impossible to afford for underdeveloped countries. Large-scale production of biodiesel from edible oils may cause negative impact to the world such as food crisis leading to economic imbalance. Hence, non-conventional and non-edible oils definitely have the advantage over edible oils as potential feedstocks for biodiesel production. In this review, various non-conventional potential feedstocks are identified and listed for use in future biodiesel industries. It is the time for all concerned to concentrate for the development and setting up of bio-refineries for large-scale production of biodiesel.

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