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PROPERTIES OF NEEM, JATROPHA, MAHUA AND KARANJA SEEDS OIL AS POTENTIAL FEED STOCKS FOR BIODIESEL PRODUCTION: A REVIEW

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ABSTRACT

Fossil fuel resources are decreasing daily while biodiesel fuels are attracting increasing attention worldwide as blending components or direct replacements for diesel fuel in vehicle engines. This study investigated the physicochemical properties of oils extracted from seeds for their suitability in biodiesel production. This is with a view to compare which of the oils has better functional properties for a quality biodiesel production. Biodiesel is an alternative diesel fuel prepared from renewable resources and is most popular as an alternative energy sources because it is non toxic and biodegradable . India has great potential for production of biodiesel from non-edible oil seeds. From about 100 varieties of oil seeds, only 10-12 varieties have been tapped so far. The promising non-edible sources in India are Madhuca Indica (Mahua) ,Jatropha curcas(Ratan Jyot), Pongamia pinnata (Karanja) and Meliaazadirachta (Neem).

Keywords- *Non edible oils, Alternative fuel, Bio diesel, Renewable energy.*

I. INTRODUCTION

The major percentages of energy used in the world today are being generated from fossil fuel sources. These fossil fuels are non-renewable resources that take millions of years to form and their reserves are being depleted faster than they are being regenerated. They are the major contributors and sources of green house gases, air pollution and global warming. Due to recent petroleum crisis and unavailability of petroleum diesel the demand for petroleum diesel is increasing day by day hence there is a need to find out an appropriate solution. Biodiesel is a clean burning alternate fuel, produced from renewable resources like virgin or used vegetable oils, both edible and non edible. It can be used in compression-ignition (diesel) engines with little or no modifications. Biodiesel is simple to use, biodegradable, nontoxic, and essentially free of sulfur and aromatics. It can be stored just like petroleum diesel fuel and hence does not require a separate infrastructure.

The use of biodiesel in conventional diesel engines results in substantial reduction of unburned hydrocarbons, carbon monoxide and particulate matters. Its higher cetane number improves the ignition quality even when blended in petroleum diesel. The use of edible oil to produce biodiesel in India is not feasible in view of big gap in demand and supply of such oil. Indian plants like Jatropha (Jatropha curcas), Mahua (Madhuca Indica), Karanja (Pongamia pinnata) and Neem (Mellia azadirachta) contain 30% or more oil in their seed, fruit or nut. Better environmental performance, greening of wastelands and creation of new employment opportunities are the main advantages of biofuels. In India, as edible oils are in short supply, non-edible tree borne oilseeds (TBOs) of karanja, Jatropha , Mahua and Neem are being considered as the source of straight vegetable oil (SVO) and biodiesel. Plant species, which have 30% or more fixed oil in their seeds or kernel, have been identified. Traditionally the collection and selling of tree-based oilseeds was generally carried out by poor people for use as fuel for lighting. Presently there is an extended use of these oils in soaps, varnishes, lubricants, candles, cosmetics, etc. However, the current utilization of non-edible oilseeds is very low. There are many ways and procedures to convert vegetable oil into a Diesel like fuel, the transesterification process was found to be the most viable process .Trans-esterification is the process of using an alcohol (e.g. methanol, ethanol or propanol), in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to break the molecule of the raw renewable oil chemically into methyl or ethyl esters of the renewable oil, with glycerol as a by product. Trans-esterified oils have proven to be a viable alternative diesel engine fuel with characteristics similar to those of Diesel fuel. Its physical and chemical properties required for operation of diesel engine are similar to petroleum based diesel fuel. Just like petroleum diesel, biodiesel operates in compression-ignition engines. Transesterification is a chemical reaction that aims at substituting the glycerol of the glycerides with three molecules of monoalcohols such as methanol thus leading to three molecules of methyl ester of vegetable oil**.** The molecular weight of ester molecule is 1/3rd of oil and low viscosity. Methanol and ethanol is widely used in the transesterification .Methanol is used because of low cost, and physicochemical advantages with triglycerides and sodium hydroxide. The alkali hydrolysis of the oil must have acid value

<1 and moisture content of <0.5%. The acid catalyst is the choice for transesterification when low-grade vegetable oil used as raw material because it contains high free fatty acid (FFA) and moisture. Acid catalyst as sulphuric acid (H2SO4) is used for esterification process.

II. NON-EDIBLE TREE BORNE OILSEEDS (TBOs)

A. Neem

Neem (Mellia azadirachta) is of Meliaceae family. The other names of neem are Margosa, Veppam, Vepun, Nimba and Vepa (Telugu) etc**[15-17]**.It is one of the two species in the genus Azadirachta, and is native to India and Burma, growing in tropical and semi tropical regions. Neem is a fast growing tree and can reach upto a height of 15 – 20 merrily to 35 – 40 m. It bears an ovoid fruit, 2cm by 1cm and each seed contains one kernel. The seed kernels, which weigh 0.2g, constitute some 50-60% of the seed weight and 25% of the fruit. The fat content of the kernels ranges from 33-45%. The fruit yield per tree is 37-55 kg.. Neem oil can be used as Soaps, medicinal and insecticide . Neem oil is usually opaque and bitter but it has recently been shown that it can be processed into non bitter edible oil with 50% oleic acid and 15% linoleum acid. The bitter cake after extraction of oil has no value for animal feeds although it has been reported that after solvent extraction with alcohol and hexane a meal suitable for animals is produced. Neem seeds are usually crushed prior to extraction in ghanis. Whole dried fruits may be directly passed to expellers. Good quality kernels (50% oil) yield 40% oil in ghanis. In expellers whole dried fruits, depulped seeds and kernels, yield 4-6%, 12-16% and 30-40% oil respectively (Bring)). The cakes, which contain 7-12% oil are sold for solvent extraction. Major fatty acid composition of oil are Palmitic acid 19.4%,Stearic acid 21.2%,Oleic acid 42.1%,Linoleic acid 14.9%,Arachidic acid 1.4%.Neem oil is unusual in containing non-lipid associates often loosely termed as "bitters" and organic sulphur compounds that impart a pungent, disagreeable odour.

B. Jatropha (Jatropha curcas)

Jatropha curcus is a drought-resistant perennial, growing well in marginal/poor soil. Jatropha the wonder plant produces seeds with an oil content of around 37%. The oil can be combusted as fuel without being refined. It burns with clear smoke-free flame, tested successfully as fuel for simple diesel engine. The by-products are press cake a good organic fertilizer, oil contains also insecticide. It is found to be growing in many parts of the country, rugged in nature and can survive with minimum inputs and easy to propagate .Medically it is used for diseases like cancer, piles, snakebite, paralysis, dropsy etc. Depending on soil quality and rainfall, oil can be extracted from the jatropha nuts after two to five years. It grows on well-drained soils with good aeration and is well adapted to marginal soils with low nutrient content. Jatropha curcas grows almost anywhere, even on gravelly, sandy and saline soils. It can thrive on the poorest stony soil. The leaves shed during the winter months form mulch around the base of the plant. 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 is also suitable for preventing soil erosion and shifting of sand dunes. The fatty acid composition of jatropha oil has been reported in **Table –2**.

C. Mahua (Madhuca Indica)

Bio diesel from mahua seed is important because most of the states of India are tribal where it is found abundantly. The annual production of mahua is nearly 181 Kt. Mahua is a non traditional, non edible oil also known as Indian butter tree. Mahua seed contain 30-40 percent fatty oil called mahua oil. Mahua is a medium to larger tree. In India the mahua plant is found in most of the state e.g. Orissa, Chatishgada, Jharkhand, Bihar,Madhya Pradesh ,Tamil nadu. It can be sucessesfully grown in waste land & dry land. The tree is a strong light demander and gets readily suppressed under shade. The tree has potential of enhancing rural income. The tree may attain a height of upto 20 meters and is well adapted to varied weather conditions it has wide spreading branches and circular crown which presents a visually appealing structure. The tree has a large spreading root system, though many of them are superficial. The fruit is a kind of berry, egg shaped. Mature seeds can be obtained during June to July. The mahua tree starts bearing seeds from seventh years of planning. Commercial harvesting of seeds can be done only from the tenth year. Seed yield ranges from 20 -200 kg per tree every year, depending on its growth and development. As a plantation tree, Mahua is an important plant having vital socioeconomic value. This species can be planted on roadside, canal banks etc on commercial scale and in social forestry program's, particularly in tribal areas. Wood can be used as timber, making pulp and paper. Mahua flowers are rich in sugar, minerals, vitamins and calcium. The fatty acid composition of mahua oil oil has been reported in **Table – 3**.

D. Karanja (Pongamia pinnata)
Karanja is a medium sized tree is found almost throughout India. Karanja tree is wonderful tree almost like neem tree. The common name of the oil is Karanja Seed Oil and the botanical name is Pongamia glabra of Leguminaceae family. Pongamia is widely distributed in tropical Asia and it is nonedible oil of Indian origin . It is found mainly in the Western Ghats in India, northern Australia, Fiji and in some regions of Eastern Asia. .The plant is also said to be highly tolerant to salinity and can be grown in various soil textures viz. stony, sandy and clayey. Karanja can grow in humid as well as subtropical environments with annual rainfall ranging between 500 and 2500 mm. This is one of the reasons for wide availability of this plant species. The tree bears green pods which after some 10 months change to a tan colour. The pods are flat to elliptic, 5-7 cm long and contain 1 or 2 kidney shaped brownish red kernels. The yield of kernels per tree is reported between 8 and 24 kg. .The kernels are white and covered by a thin reddish skin. The composition of typical air dried kernels is: Moisture 19%, Oil 27.5%, and Protein 17.4%. The present production of karanja oil approximately is 200 million tons per annum. The time needed by the tree to mature ranges from 4 to 7 years and depending on the size of the tree the yield of kernels per tree is between 8 and 24 kg. The oil content extracted by various authors ranges between 30.0 to 33% **[3]**. The oil is used by common people due to its low cost and easy availability. The fatty acid composition of karanja oil has been reported in **Table – 4**

Table 1. Annual Production of Non-edible Oil Seeds in India

Type	Production (MT)	Oil %
Neem	500	30
Karanja	200	27-39
Kusum	80	34
Pilu	50	33
Ratanjot	-	30-40
Jaoba	-	50
Bhikal	-	37
Wild Walnut	-	60-70
Undi	04	50-73
Thumba	100	21

Table 2. Fatty acid of jatropha oil

Fatty Acid	Formula	structure	Wt%
Myristic	$C_{12}H_{28}O_2$	14:0	0.5-1.4
Palmitic	$C_{16}H_{32}O_2$	16:0	12–7.0
Stearic	$C_{18}H_{36}O_2$	18:0	5.0–9.7
Oleic	$C_{18}H_{34}O_2$	18:1	37-63
Linoleic	$C_{18}H_{32}O_2$	18:2	19-41

Table 3. Fatty acid of mahua oil

Fatty Acid	Formula	Structure	Wt%
Palmitic	$C_{16}H_{32}O_2$	16:0	16.0–28.2
Stearic	$C_{18}H_{36}O_2$	18:0	20.0–25.1
Arachidic	$C_{20}H_{40}O_2$	20:0	0.0–3.3
Oleic	$C_{18}H_{34}O_2$	18:1	41.0–51.0
Linoleic	$C_{18}H_{32}O_2$	18:2	8.9–13.7

Table 4. Fatty acid of karanja oil

Fatty Acid	Formula	structure	Wt%
Palmitic	$C_{16}H_{32}O_2$	16:0	3.7–7.9
Stearic	$C_{18}H_{36}O_2$	18:0	2.4–8.9
Lignoceric	$C_{20}H_{40}O_2$	24:0	1.1–3.5
Oleic	$C_{18}H_{34}O_2$	18:1	44.5–71.3
Linoleic	$C_{18}H_{32}O_2$	18:2	10.8–18.3

III. OIL PROCESSING TECHNOLOGY OF OIL SEEDS

A. Oil extraction and Purification of Oil

Although oil extraction can be done with or without seed coat, for jatropha, utilization of a mechanical de hulling system (to remove the seed coat) can increase oil yield by 10%.Choosing efficient extraction methods can increase the yield by more than 5%. While in cold pressing (<60°C), around 86 – 88% efficiency is achieved, hot pressing (110 – 120°C) can increase it to around 90%.The solvent extraction method enhances the efficiency up to 99%. A disadvantage with the solvent extraction is that the quantity of phospholipids in solvent extracted oil is twice as high as compared to pressed oil. This necessitates a further step of oil de gumming before trans-esterification. Oil extraction methods are also being developed based on fermentation hydrolysis. In this process, cell walls of the oil plant seeds are destroyed followed by the release of the oil present within the cells. This new method not only produces higher quality of oil and cake but also requires much less energy and results in lower levels of environmental pollution. The efficiency so far obtained is 86% and more research is needed to develop an effective enzyme system. The extracted oil can be purified by Sedimentation prosesss.This is the easiest way to get clear oil, but it takes about a week until the sediment is reduced to 20 - 25 % of the raw oil volume. The purification process can be accelerated tremendously by boiling the oil with about 20 % of water.

B. Detoxification of seed cake

After extraction of oil from seed the detoxification of the seed cake is necessary so that the seed cake can be used as cattle feed. The type of toxic component present in the seedcake varies from seed to seed, but for jatropha seed cake detoxification is highly essential. From Several investigations it is found that de-acidification and bleaching could reduce the content of toxic phorbol esters to 55% . Efficiency of the treatment also depends upon the type of toxic component present in the seedcake and the effective detoxification techniques.

IV. BIODIESEL PROCESSING

There are four ways in which oils and fats can be converted into biodiesel, namely, transesterification, micro emulsions and pyrolysis. Pyrolysis refers to a chemical change caused by application of thermal energy in absence of air or nitrogen. The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. The pyrolyzate has lower viscosity, flash & pour points than diesel fuel but equivalent calorific values. The cetane number of the pyrolyzate is lower. The pyrolysed vegetable oils contain acceptable amounts of sulphur, water and sediment with acceptable copper corrosion values but unacceptable ash, carbon residue and pour point. The formation of micro-emulsions (co-solvency) is a potential solution for reducing the viscosity of vegetable oil. Micro-emulsions are defined as transparent, thermodynamically stable colloidal dispersions. A micro-emulsion can be made of vegetable oils with an ester and dispersant (co-solvent), or of vegetable oils, an alcohol and a surfactant and a cetane improver, with or without diesel fuels. The process of converting the raw vegetable oil into biodiesel, which is fatty acid alkyl ester, is termed as transesterification. There are three basic routes to biodiesel production from oil are such as base catalyzed transesterification of the oil , direct acid catalyzed transesterification of the biolipid and Conversion of the biolipid to its fatty acids and then to biodiesel.Trans-esterification being the most commonly used method. Conversion is complicated if oil contains higher amounts of FFA (>1% w/w) that will form soap with alkaline catalyst. The soap can prevent separation of the biodiesel from the glycerin fraction. Crude oil contains about more than 25 % FFA, which is far beyond the 1% level. Few researchers have worked with feedstock having higher FFA levels using alternative processes. Pretreatment step to reduce the free fatty acids of these feedstocks to less than 1% before transesterification reaction was completed to produce biodiesel. The reduction of FFA <1% is best if esterification followed by Trans-esterification.

A. Esterification

Normally most of the oils are converted into biodiesel esters using the base catalysed transesterification method. But there are certain exceptional cases wherein direct trans-esterification cannot be performed. Such cases appear in raw vegetables oils(Non edible oil) like karanja oil, mahua oil, Nim,Jatropha and sal oil, etc because these raw vegetable oils posses high free fatty acid (FFA). For determining whether the raw vegetable oils can be trans-esterified directly the acid value is the most important property that must be known. If the acid value <3 then the raw vegetable oil can be directly trans-esterified. If the acid value >3 then there is slight change in the production process. At first the oil undergoes esterification and then followed by transesterification. In the esterification process the excess of the free acid gets reacted. The remaining acid content in the oil undergoes trans-esterification. So this method is effective for oils that contain high free fatty acid (FFA) content. So the selection of acid catalyst is very important. The aim of esterification reaction is to remove water during processing otherwise seriously hurt the reaction conversions.

B. Transesterification

Transesterification also called alcoholysis is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that an alcohol is employed instead of water. Suitable alcohols include:methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are utilized most frequently. This process is widely used to reduce the viscosity of triglycerides, there by enhancing the physical properties of fuel and improve engine performance. Thus fatty acid methyl ester (also known as biodiesel) is obtained by transesterification.

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V. FUTURE OF BIODIESEL IN INDIA

Wild crops cultivated in the westland also form a source of biodiesel production in India and according to the Economic Survey of Government of India, out of the cultivated land area, about 175 million hectares are classified as waste and degraded land. Thus, given a demand-based market, India can easily tap its potential and produce biodiesel in a large scale. the annual production of non-edible oil seeds in India.**G**overnment agencies like Ministry of Rural Development, Environment and Forestry, Petroleum and Natural Gas, Agriculture, and Non-Conventional Energy Source can all play

leading roles in this program.. Industry and research institutes have also the vital role for the success and a clear supply chain mechanism with utilization plan is necessary in national level like elsewhere across the globe. research organizations should be encouraged to undertake Life Cycle Analysis exercise for bio diesel produced from varied feedstock being used India and need to quickly develop high-yielding varieties of plants for various regions .Both scientific and agricultural research bodies should be involved directly and on a regular basis to regularly enhance the efficiency levels of both production and processing of bio diesel..It is required to select and evolve quick growing and high-yield varieties and improved methods of propagation to produce better quality oil and to provide farmer's with a choice of Tree Borne Oil species that are most appropriate to local agro-climatic conditions The seed collection and the processing of raw oil could also be taken up as a cooperative movement, which has led to several success stories in India. Small and medium scale industrial sector are required to take initiative for the downstream processing of raw oil and its supply to petroleum marketing companies.

VI. CONCLUSION

A comparative study on the functional properties of oils extracted from jatropha, neem,mahua and karanja seeds for their suitability in biodiesel production, shown that all the oils can be used as raw materials to obtain biodiesel fuel of high quality and could be suitable alternative to fossil diesel. Edible oils are in use in developed nations such as USA and European nations but in developing countries the production of edible oils are not sufficient . In a country like India, there are many plant species whose seeds remain unutilized and underutilized have been tried for biodiesel production. Non-edible oil seeds are the potential feedstock for production of biodiesel in India.

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