ISSN: 2319-5967
ISO 9001:2008 Certified
International Journal of Engineering Science and Innovative Technology (IJESIT)
Volume 2, Issue 1, January 2013

Non-Edible Oil as a Source of Bio-Lubricant for Industrial Applications: A Review

Prerna Singh Chauhan, Dr. V K Chhibber

Abstract*— Vegetable oils as renewable raw materials for new industrial products such as lubricants have been a great importance now a day because of the emphasis on environmental friendly lubricants is large in demand due to the rapid depletion of world fossil fuel reverses and increasing concern for environmental pollution from excessive mineral oil use. Vegetables oils with high oleic contents are considered to be the best alternative to substitute conventional mineral oil-based lubricating oils and synthetic esters. Vegetable oils are preferred over synthetic fluids because they are more eco-friendly, renewable resources and cheaper too. In this paper the properties of vegetable oils, fatty esters, chemically modified esters and synthetic esters relevant for performance as lubricants in various industrial applications such as hydraulic oils, refrigeration oils, chainsaw lubricants, metal working fluids, engine oils, two-stroke oils has been proposed. The advantages such as high lubricity, viscosity-temperature relationship, low lubricant consumption, energy efficiency combined with public health, safety and environmental contamination, more than offset the disadvantages of initial costs in most of these applications. It has been suggested that modified and stabilized oils of wasteland and forest origin and other non-edible oils and their chemically modified derivatives can be produced at relatively cheaper cost than similar oils marketed in the developed world and can be introduced in India with immense environmental and performance benefits.

Index Terms— **Non-Edible Oils, Tree Born Oil Seeds, Bio Degradability, Trans Esterification, Bio-Lubricants.**

I. INTRODUCTION

Due to overwhelming utilization of non biodegradable resources and its scarcity in the coming future, along with its disadvantages has enforced us for the use of biodegradable resources of Indian origin. In the United States and Europe industry began to show interest in the development of vegetable oils and their chemically altered derivatives as bio-degradable lubricants and fuels with the increase in availability of large quantities of technically superior and genetically modified varieties of high oleic vegetable oils. Such development was further spurred by increasing environment awareness and the desire to preserve endangered species, which were arbitrarily being killed for their oils and fats [1, 2]. The environmental pollution is highly concern for the use of excessive petroleum based lubricants and their disposal especially in lost lubrication, military applications and in outdoor activities such as forestry, mining, fishing and agriculture hydraulic systems. Vegetable oils with high oleic content have been the prime factor to replace conventional mineral oil-based lubricating oils and synthetic esters [3]. Vegetable oils are preferred over synthetic fluids because they are renewable resources, cheaper and eco-friendly too [4]. Furthermore, vegetable oils lubricants are biodegradable and non-toxic, unlike conventional mineral-based oils [5]. They have low volatility due to high molecular weight of the triacylglycerol molecule and have a narrow range of viscosity changes with temperature. Polar ester groups are able to adhere to metal surfaces and therefore, posses' good boundary lubrication properties. In addition, vegetable oils have high solubilizing power for polar contaminants and additive molecules [6].

India has great potential for production of bio-lubricant from non-edible oil seeds. The country is endowed with more than 100 species of tree born non-edible oil .Seeds occurring in wild or cultivated yield oil in major quantities. In India the volume of vegetable oil based lubricants and esters used are very small. Their applications is limited to hydraulically operated earth-moving machinery, cutting, shaping, rolling and drawing operations in the automotive industry and hydraulic lifts , conveyors in very large industrial units such as power plants. Most of these lubricants are supplied by the OEMs along with the equipment or imported from OEM recommended manufacturers. Vegetable oils are preferred over synthetic fluids because they are renewable resources and cheaper [4]. Vegetable oils lubricants are biodegradable and non-toxic, unlike conventional mineral based oils [5]. Vegetable oils are perceived to be alternatives to mineral oils for lubricant base oils because of certain inherent technical properties and their ability for bio-degradability. Compared to mineral oils vegetable oils in general posses high flash point, high viscosity index, high lubricity and low evaporative loss [7]. The potential availability of source non-edible free borne oil seed in the country has been reported in table-1[25]. In India attempts are being made for using non-edible and under exploited oils for production of esters [Bio-gas]. The non-edible oils currently

ISSN: 2319-5967
ISO 9001:2008 Certified
International Journal of Engineering Science and Innovative Technology (IJESIT)
Volume 2, Issue 1, January 2013
being available karanja oil, Neem oil, Rice bran oil, Rapeseed oil, caster oil, linseed oil and Mahua oil [8]. TBO of Karanja, Neem, Mahua, Jatropha, and Castor are being considered as a source of straight vegetable oil (SVO) and bio-lubricant. Plant species which have 30% or more fixed oil in their seeds or kernel have been identified [9]. Traditionally the collection and selling of tree-based oil seeds was generally carried out by poor people as their occupation and fuel for lightning. Presently there is an extended use of these oils in soaps, varnishes, diesel, candles and cosmetics, etc. The current utilization of non-edible oil seeds is very low. There are several ways and procedures to convert vegetable oil into bio-degradable lubricants. The chemical modifications included acylation, epoxidation, partial hydrogenation and trans-esterification. Vegetable oils were transesterified by reacting with ethyl hexanol, which has been treated earlier with sodium. The temperature was kept near boiling point of alcohol and the reaction was refluxed. The excess ethyl hexanol was distilled off under vacuum. The lower layer was acidified to a pH of 4-5 and withdrawn. The upper oil layer dissolved in toluene was refluxed with a Dean and Stark trap to remove water. The toluene was distilled off yielding the ester. The ester was percolated over fuller's earth to remove organic acidity and obtain straw yellow product. The modified vegetable oils were characterized and Heavy Alkyl Benzene was thoroughly mixed at 80^oC. It was cooled down to 60^0C and additive was mixed and stirred for 30 minutes to finish the formulation. The vegetable oils and its esters are well known to be bio-degradable. The study show that it is possible to formulate the automotive and industrial lube oil from vegetable oil esters for application such as engine oils, two strokes oils, compressor oils, Aviation oil, metal working fluids, insulating oil, gear oil, hydraulic oil etc[8].

Table: 1

S.N.	Botanical Name	Potential million metric tons /year			Oil Content
		Seed	Oil	Cake	
1	Pongamia pinnata	0.20	0.055	0.145	27-39%
2	Azadirachta indica	0.50	0.100	0.400	28-31%
3	Jatropha curcas	0.05	0.015	0.035	30-40%
4	Scheleichera oleosa	0.08	0.025	0.055	34%
5	Salvadora oleoides	0.05	0.017	0.033	33%
6	Citrullus collocynthis	0.10	0.021	0.079	21%
7	Shorea robusta	1.50	0.180	1.320	12-13%
8	Madhuca indica	0.50	0.180	0.320	35%
9	Magnifera indica	0.50	0.045	0.455	7.5

II. BIODEGRABILITY

Biodegrability [10] is the ability of substance to be decomposed by microorganisms. A lubricant is classified as bio-degradable if its percentage degradation in a standard test exceeds a target level. Several screening tests are employed to assess the biodegradability of lubricants and additives. Table-2 gives the bio-degradability test adopted in various countries and bio-degradability of some base fluids is given in table-3.

Table: 2

	Time (hours)	Parameter measured	Criterion
Ready Biodegradability			
1.Modified AFNOROECD 301A	28	Loss of dissolved organic carbon	>70%
2.Modified sterm OECD301B	28	Production of CO_2	>60%
3.Modified MITI OECD301C	28	Oxygen demand	>60%
4.Closed Bottle OECD 301D	28	Oxygen demand	>70%
Inherent Biodegradability			
Modified semi-continuous activated sludge (SCAS)OECD302A	>28	Loss of dissolved organic carbon	>20%
Zahn- wellers EPMA test OECD 302B	28	Loss of dissolved organic carbon	>20%
Relatively primary biodegradation CEC-L-33-A-94	21	Loss of hydrocarbon infrared bands at $2930cm^{-1}$	>70% to≥90

ISSN: 2319-5967
ISO 9001:2008 Certified
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Table: 3

Types of fluids	Biodegradability (%) CEC-L-33-A-94 method
Mineral oils	20-40
Vegetable oils	90-98
Esters	75-100
Polyols	70-100
Trimelliates	0-70

The eco toxic properties of lubricating materials depends both on the base oils and on the additives that have been used for their production [11].The bio-degradability of lubricant is primarily influence by the main component that is the base oil [12,13], which accounts for 70-80% in engine oils and up to 90% in industrial lubricants. The bio-degradability of organic compounds depends on their chemical structures. Hence even esters based fluids used for the production of lubricants can differ in bio-degradability from one species to another [12]. The chemical composition (structure) of the compounds that form the composition of the base oils under goes changes during lubricant application as a result of exposure to a variety of factors for example temperature, air, metals, humidity, pressure etc. Above changes in chemical structures produces changes in the properties responsible for the behavior of the oil during service and consequently biodegradability.

III. NON EDIBLE TREE BORNE OILSEEDS (TBO)

National oilseeds and vegetable oils development (NOVOD) board is promoting, Karanja ,Neem ,Jatropha, Mahua etc and many other tree borne oilseeds, as India stands at the sixth place in the world in energy needs and overall demand of crude oil which is expected to rise annually by 6.2%upto 2013 [14].

A. Karanja (Pongamia glabra)

The Karanja tree is hardy, extremely adaptable tree found in almost all parts in India. It belongs to family leguminaceae; it is widely distributed in tropical Asia and found almost throughout India. It is highly tolerant to salinity and can be grown in various soil textures viz stony, sandy and clayey soil. Karanja can grow in humid as well as sub-tropical environment with annual rainfall ranging between 500 and 2500mm. It is non-edible oil of Indian origin and it is found mainly in the Western Ghats in India, Northern Australia, and Fiji and in some region of eastern Asia. The tree bears green pods which after some ten months change to a tan color. The pods are flat to elliptic, 5-7 cm long and contain 1 or 2 kidney shaped brownish red kernels. The yield of kernel per tree is reported between 8 and 24 Kg. The kernels are white and covered by thin reddish skin. The air dried kernels composition is moisture 19%, oil = 33.8% and protein 17.6%. The present production of Karanja oil is 200 million tons per annum. The tree mature from 4 to 7 years depending on the size of the tree the yield of kernel per tree is between 8 and 24 kg. The oil content extracted by various methods is in between 30 to 33% is given in Table-3. The oil is used for different purpose like lightning, and after sulphonation it is used in the leather tanning industries and it is used by the village people mainly due to its low cost and easy availability. The fatty acid composition of karanja oil determined by EMS is given in table-4[15][26]. After oil extraction detoxification of seed cake is necessary, from several investigations it is found that de-acidification and bleaching could reduce the content of toxic phorbol esters to 55% [16].

B. Neem Oil (Mellia Azadirachta)

Neem tree occurs in all parts of India, representing a large although scattered source of oilseeds. Neem grows wild in dry forests and is also cultivated all over India. The other names of Neem are margosa, veppam, vepun, nimba and vepa in (Telgu)[17-18]. Neem is large evergreen glabrous tree. It may become feet high and deciduous in drier areas. It is 40 to 60 feet high and has a girth of 6-8 feet. The flowering season is from January to march in western India. The fruit is ovoid and bluntly pointed. The component weight present of fruit part is pulp and skin =51.25%, Seed=40% and kernel=17%. The kernel constituting about 45% of the seed contain 40-45% oil. The fruit yield per tree is 37.55kg.Neem oil is used as soap, shampoo, medicinal and insecticide purposes. 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, 15% linoleum acid. After oil extraction, the bitter cake 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 yield 40% oil in ghanis. In expellers whole dried Fruits, developed seeds and kernels, yield 4-6%, 12-16% and 30-40% oil respectively, the cakes, which contain which contain, 7-12% oil are sold for oil extraction. Major fatty acid composition of neem oil is given in table 4[26]. Neem oil is unusual in containing non-lipid associates often loosely termed as “bitter” and organic sulphur compounds that impart a pungent, disagreeable odor.

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International Journal of Engineering Science and Innovative Technology (IJESIT)
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C. Mahua (Mahua indica)

The two major two species of the genus Madhuca (sapotaceae) found in India are Madhuca Indica (Syn Bassia latifolia, Madhuca latifolia) and Madhuca longifolia (Syn Bassia longifolia) Madhuca latifolia is a medium size to large deciduous tree found in Uttar Pradesh, Madhya Pradesh, Gujarat, and Andhra Pradesh. Madhua longifolia is a large evergreen tree commonly found in south India and the monsoon season extends from February to April.Mahua seed contain 30-40 percent fatty oil called mahua oil [19-20]. It is rich in sugar (73%) and next to cane molasses constitute the most important raw material for alcohol fermentation. The yield of 95% alcohol is 405 litres from one tone of dried flowers. The flowers are also eaten raw and cooked and used for making syrups. The mature fruits fall on the ground in May and July in the North and August and September in the South. The orange brown ripe fleshy berry is 2.5 to 5 cm long and contains one to four shining seeds. The seeds can be separated from the fruit wall by pressing. Drying and decertification yield 70% kernels on the weight of seeds. Each seed contain 2 kernels of size (2.5x1.75cm). The kernels contain 50% oil, the oil yield in a ghani is 20-30% in an expeller 34-37%. The expelled cake is solvent extracted to recover the residual oil.

D. Sal (Shorea Robuta)

The sal tree is the most famous of all the species of shorea (Dipterecarpaceae) found in India. It is a semi-deciduous, gre-garious tree, usually very large with a height of 18-30 m and girth of about 1.8-2.1m. It is found in still larger versions as also stunted form. The total area of sal forests in India is estimated at 111,500 sq km. The forests occur in two principal regions in India, the Central Indian belt and the belt at the foot of the Himalaya, the former the accounting for 90 percent of the total area under sal forest. The sal tree is a source of an oleoresin known as Sal Dammer obtained by tapping. It is a commercial resin and used mainly as incense. On dry distillation, the resin yields 41-68 percent of an oil known as Chua oil, which mainly consist of a mixture of 15 percent, 3,4 dimethoxy and propyl benzene,40 percent oxygenated aromatic compounds and26 percent azulenes. Its fatty acid composition is given in table 5. The typically dry fruit is composed of 23 percent wing, 30 percent pod and 47 percent. The dried wings are very brittle and can be easily pulled off.

E. Castor Oil (Ricinus communis)

It belongs to family Euphorbiaceae.It is widely distributed throughout only all tropical and subtropical regions, but also in many of the temperate countries of the globe. Castor oil is regarded as one of the most valuable laxatives in medicine and it is non-edible oil. Its annual production in India is 271 MT. Its fatty acid composition is given in table5.

F. Rice Bran Oil (Oryza sativa)

Oryza sativa in the family Graminaceae. Major producing regions are Asia, Africa and America. Rice bran is a by product of the pearling process of rice and comprises the pericarp, aleurone layer, embryo, and some endosperm. Crude rice bran oil is non-edible oil. Its annual production is 30 MT. Its fatty acid composition is given in table 5.

Table: 5

Characteristics	Karanja Oil	Neem Oil	Mahua Oil	Sal Oil	Castor oil	Rice Bran Oil
Saturated Acids						
C12	1.6	-	-	-	-	-
C14	7.9	-	-	-	-	0.4
C16	4.0	14.0	24.2	7.5	-	17.0
C18	2.0	19.0	24.6	47.1	0.3	4.02.7
Unsaturated Acids						
C18:1	62.0	49.0	39.8	39.1	8.2	45.5
C18:2	12.0	9.5	13.7	3.2	3.6	27.7
C18:3	5.0	-	-	-	-	-
Ricinoleic	-	-	-	-	87.6	-
Erucic	-	-	-	-	-	-

Table:6

Characteristics	Karanja Oil	Neem Oil	Mahua Oil	Sal Oil	Castor Oil	Rice Bran Oil
Kinematic Viscosity, cSt 40^0C 100^0C	 43.42 8.35	 68.04 10.15	 48.55 9.18	 41.23 7.23	 252.0 19.0	 23.75 6.06
Viscosity Index	172	134	174	173	90	222
Iodine Value	78	66	62		83	102

ISSN: 2319-5967
ISO 9001:2008 Certified
International Journal of Engineering Science and Innovative Technology (IJESIT)
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Saponification Value mg KOH/g	179	166	191	180	178	183
Acid Value mg KOH/g	22	23	39	12	<4	85
Pour Point ^{0}C	-9	+9	+13	-5	-10	-3

IV. OIL PROCESSING FROM NON-EDIBLE SEEDS

A. Extraction of Oil from Non-Edible Seeds and Its Purification

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 percent. By choosing efficient extraction methods the percentage yield of oil from non-edible seed can be increased by more than 5%. In cold pressing (< 60^{0}C), around 86-88% efficiency can be achieved, hot pressing (110-120^{0}C) can increase it to around 90%.Solvent extraction methods enhances the efficiency up to 99%. The comparison of different methods of oil extraction is given in table6. The only disadvantage of solvent extraction is the quantity of phospholipids in solvent extracted oil is twice as high as compared to pressed oil. In solvent extraction method generally n-hexane or n-heptane solvent is employed [8].

B. Vegetable Oil and Their Chemically Modified Derivatives

Most of the vegetable oils and their derivatives are rapidly bio degradable and relatively non-toxic to biota [21]. The vegetable oils as such as are glycerides of fatty acids C_{16} to C_{24}. The most abundant fatty acids being Oleic acid, linoleic acid, Palmitic acid, Stearic acid with certain exceptions such as coconut oil has large amount of lauric acid, Castor oil has 12 hydroxy oleic acid and karanja oil has oleic acid as major fatty acid constituents. All vegetable oils have excellent viscosity temperature characteristics vegetable oils which have large proportions of oleic, linoleinic, euricic acid and 12hydroxy oleic acid as constituents in addition have excellent low temperature flow properties. The lubricity properties such as friction wear and oiliness are much superior to any hydrocarbon type of lubricants. The thermoxidative stabilities of these oils are relatively poor as compared to mineral oil but can be readily by minor chemical transformations such as partial hydrogenation, conversion from cis to Trans form and doping them with appropriate antioxidants. Major cause of instability in vegetable oil based lubricants when compared to hydrocarbon type lubricants are unsaturation (double bond), ß CH group (glycerol moeity) and hydrolysis of ester group by water at elevated temperature and pressure. Chemical modification of vegetable oils by trans esterification with mono hydric alcohols removal of polyunsaturation by partial hydrogenation and epoxidation to fully saturate the double bond result in improving the thermo oxidative stability to a great extent without sacrificing low temperature flow properties in a big way while lubricity and high viscosity index are maintained. In India (21-23) large quantities of low cost vegetable oils of forest and wasteland origin are availability which can be converted easily by such means as hydrogenation, transesterification, acetylation and alkylation's into lubricant base fluids of moderate to high thermo oxidative stability, low temperature flow properties, superior viscosity-temperature and lubricity characteristics. These products are non-toxic and 92-99% biodegradable. Most of these formulated oils may require no antiwar additives or viscosity index improvers, and only relatively small quantities of dispersants and emulsifiers. The overall performance could turn out be superior to the conventional petroleum base oils. Apart from a cleaner environment, these oils are expected to provide energy efficiency, fuel economy, longer service life and better health and safety [24]. The fatty acid composition, estimated availability, and chemical treatment/conditioning are reported in table V and VI, and the physico-chemical and functional properties of these derivatives. It can be concluded that these oils can beneficially replace mineral oils in following operations in immediate future.

- Hydraulic oils and Engine oils
- Two stroke engine oils and Compressor oils
- Lubricants for generators and pump sets
- Gear, tractors and insulating oils
- Metalworking oils and Aviation oil
- Grease, both general purpose and multipurpose
- Lubricants for food processing and water management and disposal operations.

In the coming decades more than 81% of the total lubricants consumed in India should be replaced with rapidly biodegradable lubricants.

ISSN: 2319-5967
ISO 9001:2008 Certified
International Journal of Engineering Science and Innovative Technology (IJESIT)
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V. Conclusion

Large scale non-edible seeds plantations can provide energy security to the country, foreign exchange can be saved and hence it will provide employment to the rural masses. Further it will create infrastructure facilities for oil extraction, bio-mass utilization and commercialization from exiting trees. Plantation of such trees will help in maintaining ecological balance and increasing green cover. Above activities will reduce countries dependency on imported fuels and chemicals. Most mineral oil based greases should be replaced by rapidly bio-degradable greases as these can be formulated easily from vegetable oil based thickener and stabilized vegetable oils and their esters.

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