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Non-Edible Oils as Potential Source for Bio Lubricant Production and Future Prospects in India: A Review

KEYWORDS: Tree borne oilseeds, Non edible oils, Transesterification, Bio lubricant

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ABSTRACT *As the stock of fossil fuels diminishing, throughout the world and demands for energy based comforts and mobility ever increasing, so there is a need to increase bio lubricant production .Bio lubricant is an alternative lubricant different from mineral oil lubricant as it is prepared from non-conventional energy resources and is non toxic, biodegradable and eco friendly. India has great potential for production of bio lubricant from non-edible oilseeds. From about 100 varieties of oil-seeds, only 13-14 varieties have been tapped so far. The promising non-edible sources in India are Pongamia pinnata (Karanja), Melia azadirachta (Neem), Madhuca indica (Mahua), Linseed (Linium usitatissimum), Castor oil (Ricinus communis), Rice Bran oil (Oryza sativa).This review paper assesses and integrates the biological, chemical and genetic attributes of the plant and describes about the different tree borne oilseeds in India, extraction of oil from tree borne oilseeds, properties, composition and future potential of bio lubricant .The advantages, such as oxidation stability, resistance to corrosion, high lubricity, viscosity-temperature relationship, low lubricant consumption, energy efficiency combine with public health, safety and environmental contamination, more than offset the disadvantage of initial costs in most of these applications. 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, particularly in applications involving high environmental contamination safety and public health.*

INTRODUCTION

Bio lubricants are being given serious consideration as potential sources of energy in the future, particularly in developing countries like India. In the United States and Europe, industry began to show interest in the development of vegetables oils and their chemically modified derivatives as lubricants with the increase in availability of large quantities of technically superior and genetically modified varieties of 'high oleic' vegetables oils (Karanja, rapeseed, soyabean and sunflower oils). Increasing environment awareness and the desire to preserve endangered species, which were indiscriminately killed for their oils and fats [1, 2]. Over 60% of the lubricants are lost to the environment [3]. A significant lubricant market of some 9 million metric tons per year of industrial and automotive lubricants exists. There is an increasing concern for environmental pollution from excessive petroleum based lubricants use and their disposal especially in lost lubrication, military applications, and in outdoor activities such as forestry, mining, railroads, dredging, fishing and agriculture hydraulic systems [4]. Vegetable oils with high oleic content are considered to be potential candidates to substitute conventional mineral oil-based lubricating oils and synthetic esters [5]. Vegetable oils are preferred over synthetic fluids because they are renewable resources and cheaper [6]. Furthermore, vegetable oils lubricants are biodegradable and non-toxic, unlike conventional mineral-based oils [7].They have very low volatility due to the high molecular weight of the triacylglycerol molecule and have narrow range of viscosity changes with temperature. Polar ester groups are able to adhere to metal surfaces, and therefore, possess good boundary lubrication properties. In addition, vegetable oils have high solubilizing power for polar contaminants and additive molecules [8]. Biodegradable greases [9] are good candidates for food-processing and water-management machinery.

On the other hand, vegetable oils have poor oxidative stability primarily due to the presence of bis allylic protons and are highly susceptible to radical attack and subsequently undergo oxidative degradation to form polar oxy compounds. This phenomena result in insoluble deposits and increases in oil acidity and viscosity [10]. Vegetable oil also shows poor corrosion protection. The presence of ester functionality renders these oils susceptible to hydrolytic breakdown [11]. Therefore, contamination with water in the form of emulsion must be prevented at every stage. Low temperature study has also shown that most vegetables oils undergo cloudiness, precipitation, poor flow, and solidification at -10^{0}C upon long-term exposure to cold temperature [12] in sharp contrast to mineral oil-based fluids. These physical and chemical properties can be improved either using genetically modified oils or chemically modified oil with suitable combination of additives [13].In India, as edible oils are in short supply, non-edible tree borne oilseeds (TBO) of karanja, Linseed, Mahua, Neem,sal castor oil ricebran oil are being considered as the 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 [14].Traditionally the collection and selling of tree oilseeds was generally carried out by poor people for use as fuel for lightening. Presently there is an extended use of these oils in soaps, shampoos, varnishes, bio lubricants, candles, cosmetics, biodiesel, etc. However, the current utilization of non-edible oilseeds is very low. Non edible oils can be converted into bio lubricant by chemical modification which includes acylation, epoxidation, partial hydrogenation and trans-esterification [15]. Trans-esterification process was found to be most viable process [16]. Trans-esterification is the process of using an alcohol (e.g. methanol, ethanol, or ethyl hexanol), in the presence of 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 byproduct [17]. Trans-esterification 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 [18]. Table1indicates the potential availability of some non-edible tree borne oil seed in the country [19].

TABLE-1 POTENTIAL AVAILABILITY OF SOME NON-EDIBLE OIL SEEDS IN INDIA

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%

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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

Concerns over the discharge and accumulation of lubricants and fuels on land, water and air posing serious hazards to health and deleterious effects on the environment led to the framing of increasing stringent state policies discouraging the use of conventional petroleum based lubricants in several applications such as total loss lubricants, industrial lubricants for food processing, water-management machinery, two-stroke engine lubricants, etc. and encouraging their replacement with rapidly biodegradable lubricants of low toxicity [20,21]. There are moves to replace mineral oil based lubricants in high powered diesel engine vehicles with low evaporation loss ester based lubricants in order to reduce particulate emissions which pose serious respiratory problems in large cities [22, 23].

TOXICITY

The toxicity [24] of lubricants, additives and fuels is the propensity to produce adverse biochemical or physiological effects in living organisms. The typical criteria adopted for estimating toxicity are as follows:

- Aquatic oral and dermal toxicity - LD50 < 2g/kg
- Eye irritation-corneal opacity - 2 or more
- Conjunctival redness (24-72 hrs) - 2.5 or more
- Skin irritation anathema (redness) - 2.0 or more

Several test methods have been adopted in different countries to measure the criteria of toxicity of lubricants and formulated additives. A list of such methods is given in Table2 [24] and the criteria for aquatic toxicity levels based on EC values are reported in Table 3[24].

In India the volume of vegetable oil based lubricants and esters used are very small. The global lubricant market has a volume of approximately 40 million tones, of which vegetable oil based lubricants and chemically modified esters currently account for only about 10-15%. Most of this demand is concentrated in the USA, Western Europe Japan and, to a limited extent, the Far East [25].

BIODEGRADABILITY

Biodegradability [26] is the ability of substance to be decomposed by microorganisms. A lubricant is classified as biodegradable 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-4[27] gives the bio-degradability test adopted in various countries and bio-degradability of some base fluids is given in table-5[27].

TABLE-2 TEST METHODS FOR TOXICITY OF LUBRICANTS

Test methods	Bio organism	Parameters
OECD201/DIN38412(IX)	Algae	EC10,EC50
OECD202/DIN38412(II)	Daphne	EC10, EC50
OECD203	Fish	LC10,LC50,LC100
OECD209	Sludge	LC10,LC50,LC100
ISO8192/DIN38412(VII)	Bacteria	EC10,EC50

TABLE-3 AQUATIC TOXICITY LIMITS BASED ON EC50 VALUES

Category	EC50 mg/l
Relatively harmless	>1000
Practically non-toxic	>100 to 1000
Slightly toxic	>1 to 100
Moderately toxic	>1 to 10
Highly toxic	<1

German classification of fluids based on WGK numbers

Substance	WEN	WGK Number	Classification
Vegetables oil and esters	0-1.9	0	Not hazardous to water
Hydrocarbon lubricant base oils and white oils	2-3.9	1	Slightly hazardous to water
Additive treated lube oils engine oils and industrial oils	4-5.9	2	Moderately hazardous to water
Additive treated soluble oils, water miscible coolants	>6	3	Highly hazardous to water

TABLE-4 BIODEGRADABILITY TEST METHODS

Ready Biodegradability	Time (hours)	Parameter measured	Criterion
Modified AFNOROECD 301A	28	Loss of dissolved organic carbon	>70%
Modified sterm OECD301B	28	Production of CO_2	>60%
Modified MITI OECD301C	28	Oxygen demand	>60%
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

TABLE-5 BIO-DEGRADIBILITY OF SOME BASE FLUIDS

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 bio-degradability of lubricant is primarily influence by the main component that is the base oil [28, 29].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 biodegradability from one species to another [28]. 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.

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 [30].

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KARANJA (PONGAMIA GLABRA)

Pongamia glabra is from family leguminaceae is and widely distributed in dry tropical Asia. Major producing countries are India (annual production 60 MT), Philippines and East Indies. It has high oleic acid content which is required for desirable bio lubricant and is non-edible oil. The oil content extracted by various author ranges between 30.0 to 33% [31].The fatty acid compositions of karanja oil determined by EMS is given in table-6[15].

NEEM OIL (MELLIA AZADIRACHTA)

Neem tree occurs in all parts of India, representing a large although scattered source of oilseeds.Neem is of Meliaceae family. The other names of neem are Margosa, Veppam, Vepun, Nimba and Vepa (Telgu) etc [32-34]. Major fatty acid composition of neem oil is given in table 4. Neem oil is unusual in containing non-lipid associates often loosely termed as "bitter" and organic sulphur compounds that impart a pungent, disagreeable odor.

MAHUA (MAHUA INDICA)

Madhuca Indica and Madhuca Longifolia, popularly Known as illipe, mee, Madhuka, moha, mahua, mohua, mowra,mowrah, bassia, myitzu-thaka-natpau, ippe, yappa, mahuda, hippe, ponnam, maul, butter tree etc. It is widely distributed tropical Asia. Mahua seed contain 30-40 percent fatty oil called mahua oil [35-39].

TABLE-6 FATTY ACID COMPOSITION OF VEGETABLE OILS

Characteristics	Karanja Oil	Neem Oil	Mahua Oil	Linseed Oil	Castor oil	Rice Bran Oil
Saturated Acids						
C12	1.6	-	-	-	-	-
C14	7.9	-	-	-	-	0.4
C16	4.0	14.0	24.2	6.4	-	17.0
C18	2.0	19.0	24.6	4.5	0.3	2.7
Unsaturated Acids						
C18:1	62.0	49.0	39.8	21.0	8.2	45.5
C18:2	12.0	9.5	13.7	17.4	3.6	27.7
C18:3	5.0	-	-	50.6	-	-
Ricinoleic	-	-	-	-	87.6	-
Erucic	-	-	-	-	-	-

LINSEED OIL (LINIUM USITATISSIMUM)

It belongs to family Linacae. It is originated from Middle East countries and is cultivated in temperate regions of Canada, Argentina, India and USA. It is also used as non-edible oil only. Its annual production in India is 84 MT [15].

CASTER OIL (RICINUS COMMUINS)

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 is an non-edible oil. Its annual production in India is 271 MT [15], its fatty acid composition is given in table6.

RICE BRAN OIL (ORYZA SATIVA)

Oryza sativa is from 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 bram oil is non-edible oil [15]. In India its production is 30MT. Its fatty acid composition is given in table 6.

The non-edible oils currently being available as starting materials in India Include Neem oil, Karanja oil, Rice bran oil, Castor oil, Linseed oil and Mahua oil. Vegetable oils are long chain fatty acid tri esters of glycerol. The fatty acid may differ in saturation and chain length, which provide most of the desirable lubricant properties such as good boundary lubrication, high viscosity index, high flash point and low volatility Table 7 [15]. In India [40-42] largequantities of low cost vegetable oils of forest and wasteland origin are available which can be converted easily by such means as hydrogenation, transesterification, acetylation and alkylation into lubricant base fluids of moderate to high thermooxidative stability, low temperature flow properties, superior viscosity-temperature and lubricity characteristics. These products are non-toxic and 90-100% biodegradable. The purchasing cost of finished base fluids may be up to 2.5 times that of highly refined hydrocracked VHVI oils. Most of these formulated oils may require noantiwear 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 cleaner environment, these oils are expected to provide energy efficiency, fuel economy, longer service life and better health and safety. 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. Performance evaluations of various lube oil formulations were conducted to find out its suitability (Table-8) [15]. The main characteristics for evaluation were oxidation stability, Thermal stability, corrosion, deposit forming tendency on hot metal surface, lubricity Kinematic Viscosity, Flash point, Acid Value, oxidation, lubricity, etc.

TABLE-7 PHYSICO-CHEMICAL CHARACTERISTICS OF VEGETABLE OILS

Characteristics	Soluble Cutting Oil		2 T Oil		Insulating Oil		Hydraulic Oil	
	Spec	Found	Spec.	Found	Spec.	Found	Spec.	Found
Neutralization no	7	3	-	-	0.03	0.02	-	-
Ash content %	0.01	0.008	0.12	0.08	-	-	-	-
Copper corrosion	<1	<1	<1	<1	<1	<1	<1	<1
Flash Point^{0}C	160	210	>70	100	140	150	160	170
K.Viscosity 40^{0}C	15/30	27	21.1/4.5	15	27	24	19.8/24.2	24
Viscosity Index	-	-	127	150	-	155	90	170
Reactable Sulfur %	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Panel cocker test	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Pour point^{0}C	-	-	-54	<-24	-6	-24	-3	-24
Thermo-oxidative test	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Special requirement	Pass-emulsion test	Pass	Mineral Oil Compatible	Compatible	Dielectric const 30 KV	40KV		

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Study indicates that the formulations are meeting the requirements of biodegradability also. Vegetable oils and its esters are well known to be biodegradable. It is possible to formulate the automotive and industrial lube oil from vegetable oil esters for application such as Engine Oils, Two Stroke Oils, Compressor Oils, Aviation Oil, Metal Working Fluids, Insulating Oils, Gear Oils, Hydraulic Oils and refrigeration oils etc [27]. Trends in gear oil and transmission oils are currently undergoing significant change [43]. Most passenger cars, buses, and goods transport vehicles sold in the USA incorporate automatic transmission. The trends towards use of alternative refrigerants as replacements for ozone-depleting CFCs, improved heat transfer, filled-for-life refrigeration lubricants and maximization of operational efficiency has made polyol esters and diesters attractive replacement for conventional low temperature petroleum based lubricants [42]. The loss of hydraulic fluids used in agricultural machinery, earthmoving machinery, tunneling machinery, snow crawlers, and deck machinery on ships, waste trucks and road cleaners is uncontrollable and contributes severely to soil contamination because of the toxicity of conventionally used petroleum based and synthetic hydrocarbon based fluids and even phosphate esters [44].

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
Saponification Value mg KOH/g	179	166	191	180	178	183
Acid Value mg KOH/g	22	23	39	12	<4	85
Pour Point^0C	-9	+9	+13	-5	-10	-3

TABLE-8 TYPICAL SPECIFICATIONS AND CHARACTERISTICS OF FOUR BIO-LUBES

CONCLUSION

Contaminated environment is expensive. Conventional mineral oil based lubricants are extremely harmful for the biosphere when they get into the environment. Due to poor degradability mineral oils remain in the ecosystem for a long time. Even in case of high dilution the effect will be fatal (eco-toxicological effect). Higher amount will be required for elimination of contaminated ecosystem clearly. Eco friendly hydraulic oil, refrigerator oil, gear oil, motor oil, two stroke engine oils, lubricants for food processing and water management and disposal operations and eco-friendly greases for both general purpose and multipurpose should be widely used. Eco friendly biodegradable lubricants has to be immediately introduced in the market to replace the mineral oil and other non-biodegradable products currently in use in these countries to check rampant pollution caused by these lubricants. Edible oils 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 bio lubricant in India.

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