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Some Eco-friendly Biolubricants

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Abstract:

In this study efforts were made to synthesized biolubricants using crude mahua oil and karanja oil by esterification-trans-esterification and processed through trimethyopropane route to form biolubricants. Based on density, viscosity, viscosity index, pour point, flash point and acid value synthesized biolubricant better than commercial lubricant. Effect of selected biolubricants and commercial lubricants has been studied on blood of *Clarias gyriepinus* by analyzing blood samples for biochemical study. Study reveals prominent variation in titer of cholesterol and triglycerides of blood of *Clarias gyriepinus* tested with commercial lubricant than biolubricant. This shows biolubricant are less harmful to fish than commercial lubricant. The proposed compositions can be easily prepared and eco-friendly.

1. Introduction:

Vegetable based oils have a great strength and a attractive alternative for the conventional mineral oil because of their structural similarity with long chain hydrocarbons in characteristics of being renewable, non-toxic, economic and eco-friendly [1-4]. A primary motivation behind the developments of new technology is environmental awareness. Therefore, use of ecofriendly synthetic products in environmentally sensitive areas has become one of the most researched topics of the day. Development of eco-friendly base stock for the replacement of mineral oil base stock in the new generation lubricants is one of the major challenges [5-9]. The depletion of the world's crude oil reserve couple with the consumption rate, increase in petroleum prices , scarcities and issues related to conservation have brought about renewed interest in the use of bio-based material [10]. Mineral oil has provided us with efficient and cost effective lubricant over the decade but they face a big environmental threat.

Most of lubricants for industrial utility are made from non-biodegradable materials like synthetic oils or petroleum derivatives. Millions of tons of lubricating oil is discharged in water reservoirs like river and sea which in turn contaminate ground water. This is great threat to plant and aquatic life [11]. Thus it is very necessary to solve this environmental problem by doing effective research in biolubricant synthesis. Now a days plant oils, renewable resources, are findings their way into industrial and transportation applications as lubricants. Lubricants prepared from vegetable oils are reflected to as biolubricants and these are mainly triglyceride esters [12]. Biolubricants have improved thermal and cold-flow instability as compared to neat plant oils and fulfill the basic requirements as mineral lubricant base stocks. [17,18]. Biolubricants have good low temperature fluidity and although they cannot be used at extremely high temperature still they can be suitable in less extreme application [19-25].

This study was carried out with the objective of investigating the feasibility of producing biolubricant from mahua and karanja oil by conducting chemical modification on mahua and karanja crude oil. The modification involves improving some of the lubricating properties of this crude oil. The physic-chemical properties, of biolubricant were studied and compared with certain properties of commercial lubricants. FTIR analysis of Mahua, karanja oil, their methyl ester and synthesized biolubricant was performed for confirmation of final products.

Effect of synthesized biolubricant and commercial lubricant was studied on morphology of gills of *Clarias garipinus.*

2. Material and methods:

2.1 Mahua and Karanja oil (purified) were purchased from local market. Methanol 99.8% (Sigma-Aldrich), sodium methoxide, trimethylopropane (TMP) 98% (Sigma-Aldrich), sulphuric acid 97% and ethyl acetate 99.5% (Sigma-Aldrich), sodium hydroxide (Sigma-Aldrich) were used in the manufacturing process.

2.2 Physico-chemical analysis of oil samples

Mahua and Karanja oil samples were analysed for physico-chemical properties like density, viscosity, viscosity index, pour point, flash point, fire point and acid value [15,16]. Results were compared with standard values (commercial lubricant).

Table 1: Physico-chemical Analysis of Mahua and Karanja Oil

2.3 Synthesis of biodiesel

Fatty acid methyl esters (FAME) of mahua and karanja oil were prepared by two stage transesterification [13].

Esterification of oil samples

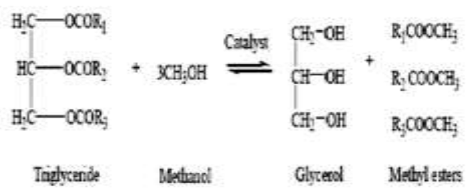
Oil esters were prepared by esterification of the oil samples (Mahua and Karanja oil) with methanol (molar ratio 1:9) using sulphuric acid as a catalyst 3.5 % (v/v) of oil.

Methyl ester synthesis (oil trans-esterification)

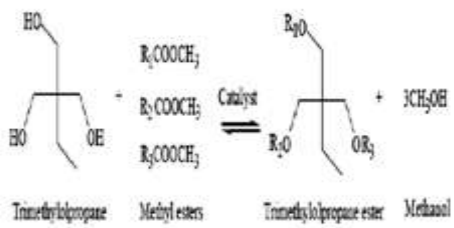
Methyl ester synthesis of esterified oil was done by base catalyzed trans-esterifiction. Reaction was carried out by using 1:9 molar ratio of oil to methanol, in presence of sodium hydroxide as a catalyst 0.8% (v/v) of esterified oil. Reaction temperature was kept around 65^{o}C in to water bath for 90 minutes at the stirring rate of 450 to 700 rpm [13]. Above transesterification was followed by several purification steps as described elsewhere (28*). The obtained methyl mahua/ karanja biodiesel was treated with silica gel for 30 minutes to remove soap, and then sample was filtered and dried overnight in an oven at 105^{0}C.

Synthesis of biolubricant (polyol synthesis)

Mahua oil base TMP esters and karanja oil based TMP esters biolubricant were prepared. Using trans esterification reaction (fig. 1) molar ratio of methyl ester (biodiesel) to TMP was 4:1 which were carried out in rotary vacuum evaporator mode (N-1HOH) (Tokyo Rikakikai Co. Ltd.) with round bottom flask 500ml. the batch weight of methyl mahua/karnaja biodiesel was 150 in all transesterification reaction experiments. Trimethylolpropane (TMP) was initially dissolved into small amount of the obtained biodiesel with the aid of heating (70-90^{0}C) and stirring to melt the crystalline solid. The known amount of TMP was then added with stirring and the mixture was heated to the operating temperature (110^{0}C) before sodium methoxide catalyst (0.8 % w/w of the total reactants) was added according to the methyl esters. The vacuum was applied gradually after addition of the catalyst to avoid spillover reaction and methanol is being continuously removed to avoid backward reaction, duration of reaction was three hour [32].



StepI



Step II

After the reaction was completed, the reaction mixture was cooled to room temperature. Ethyl acetate was added and vacuum filtered to remove the catalyst and solid materials followed by fractional distillation. The final products (biolubricant) were analyzed for their lubrication properties using ASTM standard method [29].The resulting products were confirmed by FTIR.

A set of fish *Clarias garypinnus* were exposed to concentrations of Commercial oil and bio-lubricant.4 ml concentration per 20 lit water was used and exposed for 96 hrs. Toxic effects of both the lubricants were studied on the gill morphology (*Tilapia*).

3. Result and Discussion:

3.1 Synthesis of biolubricant from mahua oil and karanja oil

Prominent constituents of mahua oil and karanja oils (crude sample oil) are glycerol ester of fatty acid. Mahua oil has little utility for edible purposes such as cooking oil. The remaining oil is used for the production of animal feed raw material, soap, margarine and oleo-chemicals karanja oil non edible oil used for soap, oleo-chemicals etc. Due to this unique nature mahua and karanja oil it shows a promising alternative as a feed stock for manufacture of ecofriendly products. In the recent years, various approaches for biodiesel production from crude vegetable oil were published [31]. Table 1 and 2 shows properties of mahua oil, karanja oil and biodiesel. The GC analysis of the obtained mahua and karanja oil methyl esters (biodiesel) is given in table 3. In MOME Palmitic acid, stearic acid are the major saturated constituent, where as oleic acid , linolic acid and polyunsaturated fatty acids are the unsaturated content.

Table 1: Physico-chemical Analysis of Mahua and Karanja Oil

Sr. No.	Properties	Mahua Oil	Mahua Oil biodiesel	Karanja Oil	Karanja Oil biodiesel	Commercial Lubricant	ASTM
1	Density (gm/ml)	0.907	0.73	0.936	0.93	0.97	ASTMD-1298
2	Viscosity@40^{0}C (cSt)	37.18	7.15	54.54	6.47	45	ASTMD-445
3	Viscosity@100^{0}C (cSt)	11.66	2.75	15.18	2.365	6.5	ASTMD-445
4	Viscosity index	325.6	299	304.9	230.5	105.4	ASTMD-2270
5	Pour Point (^{0}C)	18	5	-1	0	-15	ASTMD-97
6	Flash Point (^{0}C)	210	170	220	165	110	ASTMD-92
7	Fire Point (^{0}C)	220	178	240	170	166	
8	Acid Value (mgKOH/gm)	26.23	0.2	18.4	0.46	0.49	ASTMD-664

Table 2: Fatty acid component of biodiesel from Mahua and Karanja Oil

Sr. No.	Name of fatty acid	C: D	Mahua Biodiesel	Karanja Biodiesel
1	Oleic	C-18:1	39.1	51.59
2	Palmitic	C- 16:0	21.53	11.65

3	Stearic	C- 18:0	18.9	7.50
4	Linoleic	C- 18:2	19.55	16.64
5	Linolenic	C- 18:3	0.16	2.6
6	Myristic	C-14:0	0.08	
7	Archidic	C-20:0	0.62	1.7
8	Saturated	---	41.19	
9	Unsaturated	---	58.81	

Table 3: Physico-chemical analysis of biolubricant and commercial lubricant

Sr. No.	Properties	Mahua Oil biodiesel	Karanja Oil biodiesel	Commercial Lubricant	ASTM
1	Density (gm/ml)	0.73	0.93	0.97	ASTMD-1298
2	Viscosity@40^{0}C (cSt)	7.15	6.47	45	ASTMD-445
3	Viscosity@100^{0}C (cSt)	2.75	2.365	6.5	ASTMD-445
4	Viscosity index	299	230.5	105.4	ASTMD-2270
5	Pour Point (^{0}C)	5	0	-15	ASTMD-97
6	Flash Point (^{0}C)	170	165	110	ASTMD-92
7	Fire Point (^{0}C)	178	170	166	
8	Acid Value (mgKOH/gm)	0.37	0.64	0.49	ASTMD-664

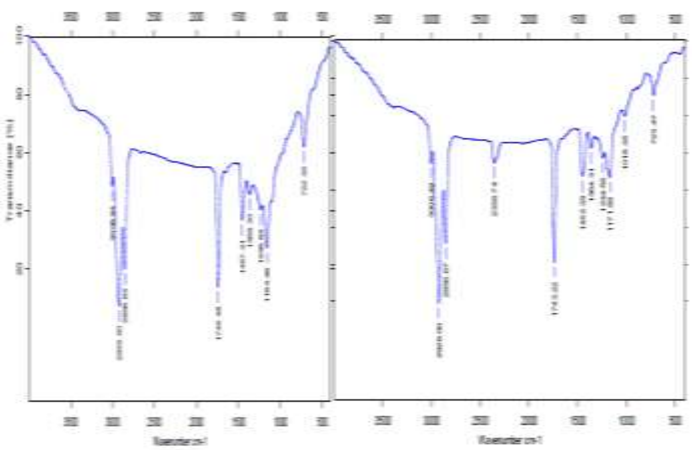
In transesterification triglycerides molecules reacts with three moles of methanol to result in glycerol and mixture of fatty acid methyl esters. Transesterification of vegetable oil derived methyl esters with polyols is the reverse process of the transesterification reaction in which glycerol is replaced by a commercial polyol. The most significant advantage of using a polyol instead of glycerol is that the absence of α- hydrogen enhance the thermal stability of lubricant at high temperature by preventing self polymerization to form free fatty acids [26].

The optimization of reaction conditions for preparation of mahua oil biolubricant was determined in another work [27]. The trimethylolpropane was chosen due to its lower melting point compared to other polyols [26]. Kinematic viscosities of mahua TMP esters were measured at 40^0C and 100^0C using viscometer as mentioned by ASTM method D445. The viscosity index (VI) was determined according to ASTM method D2270 [28]. The VI of oil is a number that indicates the effect of temperature change on its viscosity. A high VI signifies relatively little change in viscosity over a wide range of temperature. The ideal oil for most purposes is one that maintains a constant viscosity throughout different temperature changes.

In the lubricant industry, one of the critical characteristics of low temperature properties is low pour point. Determination of pour point of mahua biolubricant was conducted as per method described in ASTM D97 [26], Cis-unsaturation levels in the oleic fraction, favor decreased in pour point in vegetable oils (27). In karanja oil methyl ester (KOME) lowering in pour point is more due to higher content of oleic acid (51.59%), while in mahua oil methyl ester (MOME) pour point is high due to lower oleic acid content (39.1). Density of karanja biolubricant is greater than that of mahua biolubricant, but it is nearer to the commercial lubricant. It is due to parent chain composition of oil samples i.e. of mahua oil and karanja oil. Viscosity index of mahua biolubricant was greater than that of karanja biolubricant while the commercial lubricant has comparatively low viscosity index. The immense change is found in pour point of lubricants than crude oil samples. Decreasing the values from 18^0C to 5^0C in mahua oil lubricant, but that in karanja biolubricant it was nearly the same. Commercial lubricant was having very low pour point of -15^0C it may due to additive addition like pour point depressants. Flash point and fire point of both oil samples were higher (greater than 200^0C). In series of reaction the flash point and fire point values dropped below 200^0C. Oil methyl esters are having lowest flash and fire point than that of crude oil and final products. Significant change is caused due to the polyol synthesis reaction. Commercial lubricant is having lesser flash and fire point than that of biolubricant. The enormous decrease is achieved in acid value of biolubricants than their crude sample oil. This change is caused due to the chemical modification reaction of oils (esterification and transesterification).

Comparison of the Fourier transform infrared spectroscopy (FTIR) spectrum of both diesel and biodiesel (Fig. 1) clearly shows the similar absorption band in the region of 2855- 3000 cm^{-1} and 1350-1480 cm^{-1} due to C-H stretching vibration, which indicates the identical functional group of alkane in their molecular structure.

Fig1: FTIR spectrum for a) Mahua Oil and b) Mahua Biodiesel [32]



The FTIR spectrum of biodiesel shows new absorption band in the region of 1670-1820 cm^{-1} and there were no absorption peaks appeared at this regions for petroleum diesel. This result gave further evidence of oxygen molecule in the biodiesel product. In order to investigate the chemical compositions of mahua oil methyl ester (biodiesel) (C) mahua oil based biolubricant (b) and trimethylolpropane (TMP) (a) FTIR tests were performed and result are shown in Fig.2.

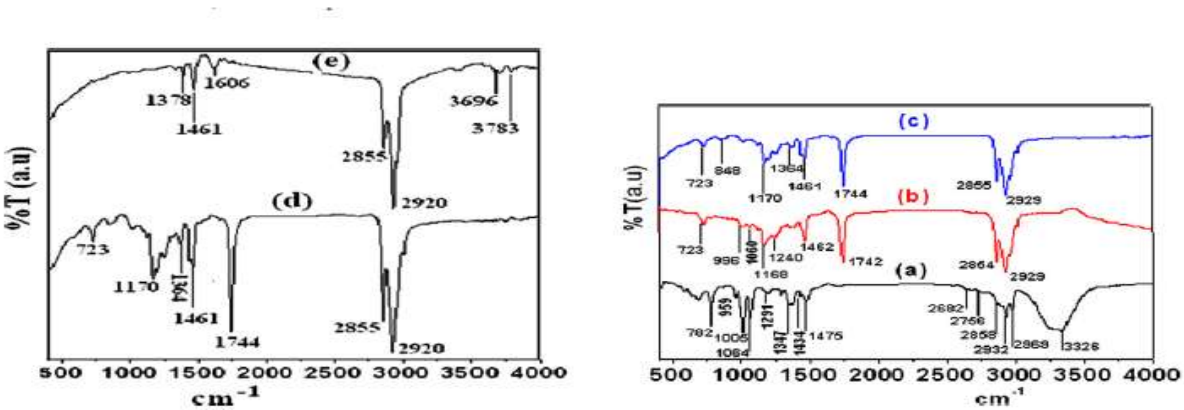


Fig. 2- FTIR spectra of (d) Mahua biodiesel; (e) Diesel oil; (a)TMP; (b) Mahua oil base biolubricant (c) Mahua oil based methyl ester [32]

The FTIR spectrum of mahua oil methyl ester and mahua oil based biolubricant shows absorption bands at 1744 cm and 1742 cm, respectively. These absorption bands are due to the C=O and C-O stretching vibration in ester which led to prove the presence of oxygen in mahua oil methyl ester and mahua oil based biolubricant. It was seen from this figure that the peak of the hydroxide group (OH) at 3326 cm^{-1} was found in TMP, while it was very small and even can be neglected at mahua oil based biolubricant (b), indicating that the biolubricant esterification reaction considerably closed to completion.

The FTIR spectrum of KOME and karanja oil biolubricant shows absorption bands at 1744 cm and 1740 cm, respectively. Theses absorption bands are due to C=O and C-O stretching vibration in both which led to prove the presence of oxygen in KOME and karanja oil biolubricant. It was seen from Fig.3 that the peak of the hydroxide group at 3326 cm was found in TMP (a) while it was very small at KOME (c) and karanja oil biolubricant (b), indicating that the biolubricant esterifiction reaction was considerably close to completion.

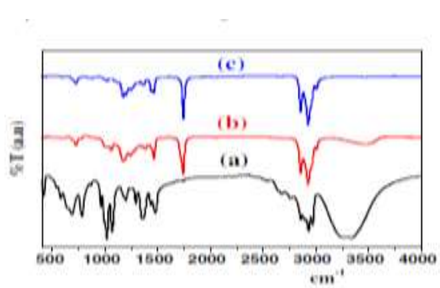


Fig.3- IR spectra of (a) TMP, b) Karanja Oil biolubricant, c) Karanja oil methyl ester [32]

The SEM studies of gills revealed abnormal gill morphology, with distinct breakages in gill arches and rackers, along with deep leisions and erosion in the epithelium. These damages were more prominent in the gill exposed with commercial lubricant, while less prominent in the gills exposed with mahua oil based biolubricant. This shows that biolubricant are less hazardous to fishes than commercial lubricant.

4. Conclusion:

The following conclusions were drawn from the above study

1) The biolubricants synthesized from karanja and mahua oil have higher viscosity index compared to the mineral oil based lubricant therefore no need of addition of viscosity index improves.
2) Lowering in pour points was observed in the biolubricant compared to crude mahua and karanja oils, though addition of pour point represent additives need to be added to again the pour point to the required values.
3) Acid values of synthesized biolubricants were closely similar to mineral oils lubricants. It prevents the addition of anti-corrosion additives.
4) Decrease in flash and fire point was achieved to match the mineral oil based lubricant properties.
5) Oxidation stability f biolubricant was supposed to be improved than mahua and karanja oil, but mineral oil is having higher oxidation stability so the oxidation, stability improver additive addition is required.
6) The FTIR spectrum of mahua and karanja oil based TMP esters (biolubricants) indicates that the biolubricant esterification reduction was considerably clone to completion.
7) As the feed oil being biodegradable, the biolubricant base oil produced was also biodegradable thus it does not harm the environment.
8) The FTIR spectrum of mahua and karanja oil based biolubricant indicates that the biolubricant esterification reaction was considerably close to completion.
9) This shows that biolubricant are less hazardous to fishes than commercial lubricant.

Thus biolubricant base stock can be successfully produced from non-edible vegetable oils which are abundantly available in India. These biolubricants can replace considerable amount of mineral oil base stocks by blending them together in different ratios. Further addition of different additives will enhanced the desirable properties of these biolubricants. These biolubricants will also help us to achieve greener future as they don't pollute the environment.

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