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Synthesis of Biolubricants from Non Edible Oils

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Abstract - *Crude mahua oil and karanja oil were analyzed for their chemical and physical properties such as density, acid value, saponification value, viscosity at 40^0c and 100^0c, viscosity index. Both the oils were then converted into oil methyl esters (biodiesel) separately by esterification and trans-esterification respectively. Each biodiesel was then processed through trimethylolpropane (TMP) route. Esterification of oil methyl ester with polyol alcohol like trimethylolpropane (TMP) yields di-esters and tri-esters. The mixture of di-esters and tri-esters is called biolubricant. Properties of resulted products which are Mahua Biolubricant and Karanja Biolubricant were found out and compared with 2T engine oil.*

Key Words: **Vegetable oil, Mahua, Karanja, Polyester, Biodiesel, Biolubricants**

1. INTRODUCTION

Innovating biobased alternatives for mineral products like fuel and lubricants has become one of the most researched topics of the day. The depletion of the world's crude oil reserve couple with the consumption rate, increase in petroleum prices and scarcities, and issues related to conservation have brought about renewed interest in the use of bio-based materials [1]. Although mineral oil has provided us with efficient and cost-effective lubricants over the decade, they pose a great deal of environmental hazard. Today most of the lubricants for industrial need are made from non-biodegradable materials such as synthetic oils or petroleum derivatives. It is well known that millions of tons of lubricating oil (Hydraulic, machinery, industrial) is discharged every year into source of water such as river and sea which contaminate groundwater. This is a great threat to plant and aquatic life [2].

It is very important to find solution for this environmental problem by making good research in biolubricant synthesis. Bio-based lubricants have begun to replace non-biodegradable fossil based mineral lubricating oils. We can significantly reduce carbon footprints by using biolubes than mineral oils.

Lubricants were synthesized from plant oils and other environmentally friendly sources which are referred to as biolubricants and these are primarily triglyceride esters derived from plants and animals. There is an increasing demand for environmentally compatible lubricants, particularly in areas where they can come into contact with water, food or people. Lubricants are generally composed of a majority of base oil plus a variety of additives to impart desirable characteristics. Lubricants are generally based on one type of base oil, but mixtures of the base oils are also used sometimes to meet performance requirements.

The quest for renewable energy sources has since dominated most manufacturing industries with much emphasis on bio products. Several researchers have agreed on the possibility of obtaining more efficient lubricants from such (bio products) sources. Hence, there is need to investigate the possibility of obtaining an environmentally friendly and economically viable lubricant from one of such sources (mahua and karanja oil). This study was carried out with the objective of investigating the feasibility of producing biolubricant from mahua and karanja oil by conducting chemical modifications on the Mahua and Karanja crude oil. The modification involved improving some of the lubricating properties of these crude oils. The physicochemical properties of Mahua and karanja biolubricant were also compared with a certain standard properties of lubricants [1]

2. MATERIALS AND METHODS

The materials and reagents used in carrying out the research are as follows: crude mahua oil, crude karanja oil, methanol, sulfuric acid, sodium hydroxide, trimethylolpropane (TMP), sodium methoxide.

The instruments and equipments used in carrying out this study are: water bath, mechanical stirrer, two neck round bottom flask, water condenser, magnetic stirrer with heating plate, Ostwald viscometer(C type), paraffin bath, pipettes, burette, test tubes.

On the basis of methodology, the research is subdivided into four categories.
2.1 Characterization of the crude oil
2.2 Biodiesel synthesis
2.3 Biolubricant synthesis
The following steps were followed as methodology.

2.1 Characterization Mahua oil:

- Density
- Viscosity
- Pour point
- Saponification Value
- Acid Value

2.2 Biodiesel synthesis

Oil Esterification:

The high FFA content of the oil was reduced by the esterification of the oils with methanol using sulphuric acid as catalyst. 250ml of the oil samples was weighed and transferred into a two necks round bottom flask. The molar ratio of oil to methanol was kept 1:9. The amount of catalyst required is 3.5% (v/v) of oil. Mechanical stirrer was inserted through one of the necks while the other neck was attached with reflux straight water condenser. The dimmer attached to stirrer was set up to 60-65V for mechanical stirring of rpm nearly 700-1000rpm. The temperature of the bath was maintained at 65^{0}C for homogeneity. The reaction mixture was kept in this conditions for about 90 minutes. After reaction was over the reaction mixture was kept in separating funnel for nearly 20 hrs. Two layer obtained were esterified mahua oil and glycerol [5].
The reactor setup is as shown in Fig 1.

Calculations for Mahua oil esterification:
Saponification value = 185.13
Molecular weight of Mahua oil was calculated with the help of saponification value as,
= 909.10gm/mole

250 ml of Mahua oil weights 218 gm.
For 218 gm of Mahua oil the amount of methanol required was calculated as,
Moles of Mahua oil = Weight of mahua oil/ molecular weight of oil
=218/909.1
= 0.2397 moles
Therefore, following the oil to methanol ratio 1:9, moles of methanol required
= 9×0.2397
Moles of methanol = 2.157
Weight of methanol required = 69.03gm

Amount of conc. sulphuric acid required 3.5% (v/v) of oil, which was 8.75ml.

Oil Trans-esterification (Methyl ester synthesis):

The methyl ester synthesis of esterified oil was done by trans-esterification reaction. This reaction was base catalysed reaction. This reaction was also accounted for decreasing the acid value of oil. Reaction was carried out by using 1:9 molar ratio of oil to methanol, in presence of sodium hydroxide as a catalyst. Catalyst amount taken was 0.8% of oil obtained in the esterification reaction. Reaction temperature was kept around 65^{0}C in water bath for 90 minutes at the stirring rate of 450-700 rpm [5].
After the reaction was over, reaction mixture is kept in a separating funnel for nearly 20 hrs.

Calculations for Mahua oil Trans-esterification:
Weight of esterified oil obtained = 223 gm (255 ml)
Weight of Glycerol = 80.23 gm

According to the molar ratio of oil to methanol 1: 9,
Amount of methanol taken = 70.64 gm (89.191 ml)
Amount of catalyst i.e. NaOH = 0.8 % of 223 = 1.784gm

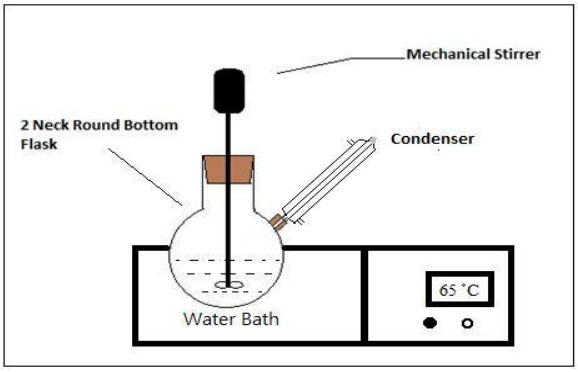

Fig 1: Esterification and trans-esterification reaction setup

Same procedure was followed for karanja biodiesel synthesis.

2.3 Biolubricant synthesis (Polyol Synthesis)

This was achieved by trans-esterification of the mahua methyl ester with trimethylolpropane (TMP) in 50 gm batch using sodium methoxide (in 30% methanol) as catalyst. The molar ratio of mahua oil methyl ester-to-trimethylolpropane was 4:1, the amount of catalyst used was 0.8% w/w of the total reactants and the reaction was conducted at a temperature of 110 ^{0}C for three hours (3 hours) in oil bath along with the stirring arrangement. The reaction was carried out under vacuum condition to promote a forward reaction by ensuring the entire methanol produced was removed from the reaction mixture. The actual reactor setup is as shown in Fig 3.

The polyester synthesis reaction is as shown in Fig 2. TMP and Oil methyl ester reacts with each other in presence of sodium methoxide catalyst at 110 ^{0}C and vacuum conditions,

to give TMP tri-esters which is a biolubricant. Methanol is being continuously removed from reaction mixture to avoid backward reaction [6].

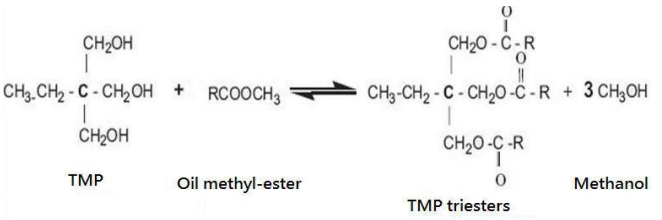

Fig 2: Polyester synthesis reaction

Calculation for Mahua polyester synthesis**:**
Mahua methyl ester to TMP ratio is taken 4:1,
For 50gm of Mahua methyl ester weight of TMP is 1.29 gm
Amount of catalyst used was 0.8 % of total reactants = 0.41gm

3. RESULTS AND DISCUSSION

3.1 Preliminary Analysis of mahua and karanja oil

Following table 1 shows the preliminary analysis of sample oil. Table includes the physico-chemical properties of Mahua oil like density, viscosity index, pour point, flash point, fire point, acid value

Table 1: Preliminary Analysis of Mahua and Karanja oil

Sr No.	Properties	Mahua oil	Karanja oil
1	Density	0.907 gm/ml	0.936 gm/ml
2	Viscosity @40^{0}C	37.18 cSt	54.54 cSt
3	Viscosity @100^{0}C	11.66 cSt	15.18 cSt
4	Viscosity index	325.6	304.9
5	Pour Point	18^{o}C	-1^{0}C
6	Flash point	210^{0}C	220^{0}C
7	Fire point	220^{0}C	240^{0}C
8	Saponification Value	185.13 mg KOH/g	188.5 mg KOH/g
9	Acid Value	26.23 mg KOH/g	18.40 mg KOH/g

All the physio-chemical properties of sample Mahua oil and karanja oil were nearly same as that of standard values [7][8].

3.2 Biodiesel properties

Table 2: Properties of methyl ester

Sr No.	Properties	Mahua Methyl ester(Prepared)	Karanja methyl ester(prepared)	Mahua methyl ester (from research paper)	Methyl Ester EN 14214
1	Density	0.98 gm/ml	0.99 gm/ml	0.872	8.6-9
2	Viscosity @40^{0}C	6.765 cSt	6.49 cSt	3.9	3.5-5
3	Viscosity @100^{0}C	3.025 cSt	3.135 cSt	----	----
4	Viscosity index	447.4	532.7	----	----
5	Pour Point	0^{o}C	-4^{0}C	----	----
6	Flash point	150 ^{o}C	140^{0}C	205	>120
7	Fire point	165 ^{o}C	148^{0}C	218	----
8	Acid Value	0.2 mg KOH/g	0.46 mg KOH/g	0.5	<0.50

The fuel properties of Mahua and karanja biodiesel are summarized in Table 2. It can be seen that these biodiesels have comparable fuel properties with those of within the limits prescribed in the latest American and European standards for biodiesel [5][9].

Methyl ester is then further reacted with TMP and Biolubricant base stock is produced having properties as shown in table 3.

3.3 Biolubricant properties

Table 3: Properties of Biolubricant synthesized using TMP

Sr No.	Properties	Mahua Biolubricant	Karanja biolubricant	2T engine oil
1	Density (gm/ml)	0.73 gm/ml	0.93 gm/ml	0.97 gm/ml
2	Viscosity @40°C (cSt)	7.15 cSt	6.47 cSt	45 cSt
3	Viscosity @100°C(cSt)	2.75 cSt	2.365 cSt	6.5 cSt
4	Viscosity index	299	230.5	105.4
5	Pour Point (°C)	5°C	0°C	-15°C
6	Flash point (°C)	170°C	165°C	110°C
7	Fire point (°C)	178 °C	170°C	116°C
8	Acid Value (mg KOH/gm)	0.37 mg KOH/g	0.64 mg KOH/g	0.49 mg KOH/g

In table 3, density of Karanja biolubricant is quite greater than that of Mahua biolubricant, but it is nearer to the 2T engine oil. This is due to the parent chain composition of sample oils i.e. of Mahua and Karanja oils.

The viscosity change occurred in both the oil biolubricants during all the intermediate products and the final, though viscosity index was high in oil methyl esters than in sample oil and final products. Viscosity index of Mahua biolubricant is greater than that of Karanja biolubricant while the 2T oil has comparatively low viscosity index.

The immense change is found in pour point of lubricants than crude sample oil. Decreasing the values from 18°C to 5°C in Mahua oil lubricant, but that in Karanja biolubricant it was nearly the same. 2T oil is having very low pour point of -15°C it may due to additive addition like pour point depressants.

Flash point and fire point of both crude Karanja and Mahua oils were higher (greater than 200°C). In series of reaction the flash and fire point values dropped below 200°C. Oil methyl esters are having lowest flash and fire point than that of crude oil and final product biolubricants. Significant change is caused due to the polyol synthesis reaction. 2T oil is having very lesser flash and fire point than that of biolubricants.

The enormous decrease is achieved in acid values of biolubricants than their crude sample oil. This change is caused due to the chemical modification reaction of oils i.e. esterification and trans-esterification. The acid value of Mahua oil is dropped to 0.37 mg KOH/gm from 26.23 mg KOH/gm, while that of Karanja biolubricant is having acid value of 0.64 mg KOH/gm which was earlier 18.40 mg KOH/gm. 2T oil is also having acid value in between this range i.e. 0.49 mg KOH/gm.

4. CONCLUSION

The following conclusions were drawn from the above study:

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

1) The synthesized biolubricant of Karanja and Mahua oil have higher viscosity index compared to the mineral oil lubricant, therefore no need of addition of viscosity index improvers.

2) Decrease in pour points was also observed in the biolubricant compared to sample oils, though addition of pour point depressant additives need to be added to again drop the pour point to the required values.

3) Acid values of synthesized biolubricants were closely similar to mineral oil lubricants. It prevents the addition of anti-corrosion additives.

4) Decrease in flash and fire point was achieved to match the mineral oil based lubricants properties.

5) Oxidation stability of biolubricant was supposed to be improved than sample oil, but mineral oil is having higher oxidation stability so the oxidation stability improver additive addition is required.

6) As the feed oil being biodegradable, the biolubricant base oil produced was also biodegradable thus it does not harm the environment.

REFERENCES

[1] Bilal S, Mohammed-Dabo I, Nuhu M, Kasim, S. A, Almustapha I. H and Yamusa Y. A, "Production of biolubricant from Jatropha curcas seed oil", Journal of Chemical Engineering and Materials Science, Vol. 4(6), pp. 72-79, September 2013

[2] Nazrizawati Ahmad Tajuddin, Nor Habibah Rosli, Noraishah Abdullah, Mohd Firdaus Yusoff, Jumat Salimon, "Estolide ester from ricinus communis l. Seed oil for biolubricant purpose", The Malaysian Journal of Analytical Sciences, Vol 18 No 1 (2014): 85 - 93

[3] Amit Kumar Jain, Amit Suhane, "Research Approach & Prospects of Non Edible Vegetable Oil as a Potential Resource for Biolubricant - A Review", Advanced Engineering and Applied Sciences: An International Journal, 2012; 1(1): 23-32

[4] H.M. Mobarak, E.NizaMohamad, H.H.Masjuki, M.A.Kalam, K.A.H.Al Mahmud, M. Habibullah, A.M.Ashraful, "The prospects of biolubricants as alternatives in automotive applications", Renewable and Sustainable Energy Reviews33(2014)34–43.

[5] Hariram V and Vagesh Shangar R, "Characterization and Optimization of Biodiesel Production from Crude Mahua Oil by Two Stage Transesterification", American Journal of Engineering Research (AJER), Volume-03, Issue-11, pp-233-239.

[6] Noor Hafizah Arbain and Jumat Salimon, "Synthesis And Characterization Of Ester Trimethylolpropane Based Jatropha Curcas Oil As Biolubricant Base Stocks", Journal of Science and Technology, Vol 2, No 2 (2010) pg 47-58.

[7] Padhi, S.K., Singh, R.K, "characterization of mahua oil (madhuca indica) for the preparation of biodiesel (mahua oil methyl ester", international conference on advances in energy research.

[8] Bobade S.N., and Khyade V.B., "Detail study on the Properties of Pongamia Pinnata (Karanja) for the Production of Biofuel", Research Journal of Chemical Sciences, Vol. 2(7), 16-20, July (2012)

[9] En 14214:2003 (e) automotive fuels-fatty acid methyl esters (fame) for diesel Engines-requirements and test methods. http://www.aascarburants.com/assets/files/pdf/Biodiesel-EN14214.pdf