

TRANSESTERIFICATION OF METHYL ESTERS OF NON-EDIBLE OILS FOR SYNTHESIZING BIOLUBRICANTS

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ABSTRACT: The growing awareness for achieving a pollution free environment has gained significant importance in green technology to synthesize 'eco-friendly' biobased products.

In this paper efforts have been made to manufacture lubricants that are biobased and hence biodegradable in nature. The chemical and physical properties such as density, acid value, saponification value, viscosity at 40°C and 100°C, viscosity index of crude Mahua oil and Karanja oil were analyzed. Such oils with the high oleic acid content are considered to be the best alternative source to substitute the mineral oil based lubricating oils. Esterification and Transesterification process was used to convert the oils into oil methyl esters (biodiesel). Further esterification of oil methyl ester with polyol alcohol like trimethylolpropane (TMP) was carried out. The mixture of these di-esters and tri-esters which is obtained is called bilubricant. Properties of resulted products which are Mahua Biolubricant and Karanja Biolubricant were found out and compared with 2T commercial engine oil.

Key-words: Mahua oil; Karanja Oil; Biodiesel; Biolubricant; Transesterification; TMP

INTRODUCTION:

Lubricants: A lubricant is a substance introduced between two surfaces in relative motion in order to reduce the friction between them and the wear induced by contact easing smoother working, cutting down the risks of undesirable frequently encountered failures and maintaining reliable machine operations. Lubricants are basically solutions or colloids that include a lubricating solvent or base fluid with functional additives that improve its lubrication properties.

The property of a lubricant which prevents its contact between the bearing surfaces is its viscosity and hence it is considered as the chief characteristic. Other important characteristics are compatibility, toxicity, chemical stability, corrosiveness, flammability, environmental effects, availability, temperature stability and price.

The basestocks may be of petroleum, vegetable or synthetic nature. Mineral oils are derived from petroleum and represent about 95% of the lubricants market in the world [1].

Millions of tons of lubricating oil (Hydraulic, machinery, industrial) is discharged every year into sources of water such as river and sea. This is a great threat to plant and aquatic life hence it is very important to find solution for this environmental problem by shifting to substitutes like bio-based lubricants [5]. Replacing the mineral oil based lubricants with bio-based lubricants can significantly reduce carbon footprints.

Biolubricants : Bio-lubricant is synthetic oleo chemical esters normally plant origin, synthesized from esterification or transesterification. Biofuels are being given serious considerations as potential sources of energy in the future, particularly in developing countries like India. As India is endowed with over 100 species of non-traditional oils, some development works have been carried out by the government of India for producing biodiesel from non traditional oils like Jatropha, Mahua and Karanja. Biodiesel from Mahua is important because most of the states of India are tribal where it is found abundantly. 30-40% of fatty oil can be extracted from mahua seeds. Nature of the oil used significantly affects the properties of the biodiesel [6]. These oils have good lubricating properties and high viscosity indices and therefore, they are being more closely examined as base oil for biolubricants.

The main objective to carry out this study was to obtain methyl esters from mahua oil and further to convert these mahua methyl esters into bio-lubricant 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.

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.

The experimental procedure can be categorized under the following heads:

- Characterization of the crude oil
- Biodiesel synthesis
- Biolubricant synthesis

EXPERIMENTAL PROCEDURE

I. Oil Characterization :

This analysis of oil gives the basis for the oil characterization to determine whether the oil could be used as lubricant base. The analysis was done for Mahua Oil which includes:

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

II. Biodiesel Synthesis:

This part is further divided into two parts as:

- Oil Esterification
- Trans-esterification of esterified oil.

➤ **Oil Esterification** : In a two neck round-bottomed flask measured quantity of oil was taken to which required amount of methanol and sulphuric acid were added. This mixture was heated by supplying heat with the help of an electric heater. During the heating process the reaction mixture was continuously stirred to maintain a constant temperature for 1-1.5 hrs. At regular interval of time samples were collected from the reaction mixture and its acid value was determined [2]. As soon as the acid value had reduced to the desired value, the products were cooled and separated by gravity settling. The reactor setup used is as shown in Fig:1.

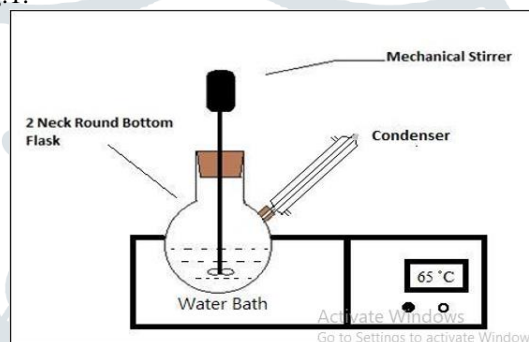


Figure-1: Esterification and Trans-esterification reaction setup

➤ **Transesterification** : The non-edible esterified oil was taken in a two neck round-bottomed reaction flask. Required amount of methanol along with KOH was added slowly to the reaction flask. The reaction mixture was heated to maintain a temperature near the boiling point of the alcohol (65°C) [2]. Similar reaction kinetics as that in the first step was maintained. In order to ensure complete conversion of the oil into esters excess amount of methanol was used. It was made sure that there were no losses of methanol vapors. After the reaction had completed the contents of the reactor were cooled and transferred into a separating funnel. The top fraction that was obtained was collected, water washed and heated to obtain Mahua Methyl Esters.

III. Biolubricant Synthesis:

Synthesis of triester is carried out by reaction of Mahua oil methyl ester with Trimethylolpropane in a proper molar ratio. The reaction was carried out in 50ml batches. Sodium methoxide was used as the catalyst. In a 250ml conical flask the reactants were continuously mixed and heated at around 100-140°C using magnetic stirrer with a heater. Partial vacuum was applied to the assembly for continuous removal of methanol and the vapors were condensed using a water condenser. A 2-3 hours of reaction time was allowed. Completion of reaction was confirmed when methanol was obtained in condenser. Similar procedure was carried out for Karanja oil. TMP triesters (biolubricant) were obtained which were tested for their properties [3].

RESULTS AND DISCUSSION:

The chemical and physical properties such as density, acid value, saponification value, viscosity at 40°C and 100°C, viscosity index of crude Mahua oil and Karanja oil were analyzed and the value obtained are specified in **Table-1**.

➤ **Table-1: Physico-chemical properties of sample Mahua and Karanja oil**

Sr. No	Properties	Mahua Oil	Karanja Oil
1.	Density	0.88g/ml	0.927g/ml
2.	Viscosity @ 40°C	37.66cSt	38.79cSt
3.	Viscosity @ 100°C	11.66cSt	8.02 cSt
4.	Viscosity Index	173.69	155.22
5.	Pour Point	20°C	9°C
6.	Saponification Value	189.33	169
7.	Acid Value	55.32 mg KOH/g	36.52mg KOH/g

The final product that was obtained after the experimental procedure was tested for various important properties and these values were compared with commercially available 2T Engine Oil. **Table-2** shows the comparison between properties of biolubricant with 2T Engine Oil.

➤ **Table-2 : Comparison of properties of Biolubricant using TMP with commercial 2T Engine Oil.**

Sr.No	Properties	Mahua Biolubricant using TMP	Karanja Biolubricant using TMP	Commercial 2T Engine Oil
1.	Density g/ml	0.96	0.924	0.97
2.	Viscosity (cSt) at 40°C	70.1	69.53	45
3.	Viscosity (cSt) at 100°C	9.76	8.98	6.5
4.	Viscosity Index	123.39	111.597	105.04
5.	Pour Point (°C)	8	6	-15.00
6.	Acid Value (mg KOH/g sample)	0.33	0.47	0.49

CONCLUSION:

- The synthesized Mahua biolubricant had a greater viscosity index than that of Karanja biolubricant while the mineral oil based 2T engine oil has comparatively low viscosity index therefore viscosity index improvers are not required in the synthesized biobased lubricants.
- Though decrease in pour points was observed in the biolubricant compared to sample oils, pour point depressant additives need to be added to again drop the pour point to the required values.
- Acid values of synthesized biolubricants were closely similar to mineral oil lubricants. It prevents the addition of anti-corrosion additives.
- Since the feed for the synthesis of biolubricant is biodegradable, the synthesized biolubricant is therefore also biodegradable, hence it does not harm the environment.

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