Synthesis of Environmental Friendly Biolubricant : A Novel Approach

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Abstract- The basic purpose of lubricant is to reduce friction between the surfaces that are moving and this property is termed as lubricity. Traditional petroleum based lubricants are the major source of pollution all over the world more over depletion of crude oil reserves and increasing crude oil prices is another area of concern. The use of environmentally acceptable bio-based lubricants has many advantages as they are biodegradable, non toxic and derived from renewable sources.

In this study the Esterification reaction of Oleic acid (generally considered to be the predominant fatty acid in nature constitutes 50% or more of the total acids of many fats) and Iso amyl alcohol is performed in the presence of perchloric acid as a catalyst and the lubricating properties of the iso amyl oleate are estimated.

Keywords – *Lubricant, biobased, lubricating properties*

I. INTRODUCTION

The major content of the lubricant is base oil that is almost 80% remaining are the additives which improve the lubricating qualities of lubricant as a result, the base oil mainly determines lubricant properties such as oxidative stability, low-temperature flow properties and lubricity. There are mainly three types of base oils : mineral oils, synthetic oils and vegetable oils. Normally , over 85% of base oils are refined from crude petroleum; however, with the depleting stocks of petroleum and high costs of synthetic lubricant, vegetable oils are considered to be potential candidates to supply high quality lubricant base oil for lubricant production. Vegetable oils have many advantages over other raw materials, as they are readily available, relatively low cost, renewable and environmentally friendly. In the present study base oil of iso amyl oleate is prepared with the reaction of oleic acid and iso amyl oleate using perchloric acid as catalyst and lubricating properties of base oil such as flash point, pour point, viscosity index are also estimated and suitability of iso amyl oleate as lubricating base oil is evaluated.

II. LITERATURE SURVEY

Ozgulsum et al.[2] investigated the esterification of oleic acid with a fraction of fusel oil. They determined the variables such as temperature, molar ratio of oleic acid to alcohol and amount of catalyst that affect yield of ester. **Lacaze-Dufaure**[3] investigated the para-toluene sulfonic acid (p-TSA) catalysed and uncatalysed esterifications between oleic acid and 2-ethylhexanol. The reactions were carried out in the presence of the stoichiometric amount or twice the stoichiometric amount of alcohol with respect to the fatty acid, at 140-170^{o}C. **Wagner et al.**[4] suggested that Lubricants based on renewable raw materials and their derivatives are drawing increased attraction in various applications. They also mentioned alternative routes to improved rapidly biodegradable base fluids, e.g. breeding successes with high oleic sunflower oil.

Hwang et al.[5] Prepared synthetic lubricant basestocks from epoxidized soybean oil (ESO) and 2-ethylhexanol (2-EH) to be used alone or with polyalphaolefin (PAO). Sulfuric acid-catalyzed reaction of ESO with 2-EH involves a ring-opening reaction at the epoxy group followed by transesterification at the ester group. They also examined the reaction with other catalysts including p-toluenesulfonic acid, Dowex 50W-8X, boron trifluoride, and sodium methoxide was also examined. **Dermo et al.**[6] prepared biolubricant by an esterification reaction of fusel oil and oleic acid in integrated system, by using immobilized Novozysm 435 lipase enzyme as biocatalyst. **Koszorz et al.**[7] studied enzymatic esterification of oleic-acid and i-amyl alcohol. The product of this reaction, i-amyl-oleate, is widely used as a bio-lubricant. During the esterification reaction, water is produced as a by-product, which has a disadvantageous effect on the reaction rate and enzyme activity.

Hong et al.[8] presented the enantioselective esterification of racemic ibuprofen catalyzed by *Candida rugosa* lipase in isooctane was coupled with pervaporation of water by-produced by the reaction. **Sreeprasanth et al.**[9] reported that the application of Fe-Zn double-metal cyanide (DMC) complexes as solid catalysts in the preparation of fatty acid alkyl esters (biodiesel/biolubricants) from vegetable oils. **Pettersson et al.**[10] reported that future lubricants have to be more environmentally adapted, have a higher level of performance, and lower total life cycle cost than presently used lubricants. **Laszlo et al.**[11] suggested that fusel oil is a bi-product of distilleries and i-amyl alcohol is its main component which can form ester compounds. They studied the esterification of oleic acid acid and i-amyl alcohol by candida antarctica lipase B in n-heptane solvent.**Elzbieta Beran**[12] reported that Biodegradability analysis of lubricants by standardised tests provides valuable information for both legislation purposes and assessment of how chemical structure influences biodegradability. **Deshmane et al.**[13] suggested that the esterification is one of the most preferred synthesis routes for organic esters which are most frequently used as plasticizers, solvents and perfumery and flavour chemicals. Their work deals with acid catalyzed synthesis of isopropyl esters from palm fatty acid

Alejandrina et al.[14] reports laboratory results obtained from the production of polyols with branched ether and ester compounds from epoxidized vegetable oils pertaining to annual, temperate climate crops (soybean, sunflower and high-oleic sunflower oils), focusing on their possible use as components of lubricant base stocks. **Sridhar et al.**[15] suggested that Fatty acid esters are useful functional molecules in pharmaceutical, cosmetic and lubricant industries. The conversion of esters may be enhanced by continuous removal of the water produced during the esterification process which is a reversible reaction. **Hafizah Arbain**[16] conducted the Biolubricant production of trimethylolpropane ester (ET) via esterification of fatty acid (FA) of Jatropha curcas oil with trimethylolpropane (TMP). **Salimon et al.**[17] prepared Synthetic biolubricant basestocks with improved low temperature and oxidative stability by chemical modification of epoxidized oleic acid (EOA). **Salimon et al.**[18] suggested that increasing pollutants in the environment lead to an increase in the use of plant oil based biolubricants. These products could lead to a significant reduction in environmental pollution and thus contribute to the discovery of a replacement for petroleum-based lubricants.

Akerman et al.[19] suggested that Biolubricants derived from vegetable oils are environmentally compatible products due to their low toxicity and good biodegradability.

Akerman et al.[20] reported that the Synthetic esters based on polyols and fatty acids possess suitable technical and ecological properties for applications as biolubricants, and can replace the mineral oil based lubricants in several applications. They synthesised trimethylolpropane (TMP) esters with oleic acid using immobilised lipase B from *Candida antarctica* (Novozym®435). TMP-trioleate has suitable properties for use as hydraulic fluids, especially at extreme temperatures. **Faiz M. et al.**[21] suggested that jatropha oil has good potential as the renewable energy as well as lubricant feedstock. **Korlipara et al.**[22] prepared a new class of polyol esters by esterification of 10-undecenoic acid (UDA) with three polyols namely trimethylolpropane (TMP), neopentyl glycol (NPG) and pentaerythritol (PE) in 92–96% yields. **Salimon et al.**[23] presented a series of chemically modified biolubricant basestocks derived from ricinoleic acid. The reactions were monitored and products were confirmed by NMR and FTIR. The synthesis protocol is carried out in three stages: (1) epoxidation of ricinoleic acid; (2) synthesis of 10,12-dihydroxy-9-acyloxystearic acid from epoxidized ricinoleic acid; (3) esterification of the acyloxystearic acid products with 2-ethylhexanol to yield 2-ethylhexyl-10,12-dihydroxy-9-acyloxystearate. They measured viscosity index, flash point, pour points (PP), and oxidative stability of the resulting products. The resulting esters could plausibly be used as bio-based industrial materials in biolubricants, surfactants, or fuel because they have improved physicochemical properties.

Salimon et al.[24] suggested that a new class of environmentally acceptable and renewable biolubricants based on plant oils is available for environmental reasons, as well as the dwindling source of petroleum. **Salimon et al.**[25] suggested that in the concepts for new products, performance, product safety, and product economy criteria are equally important. They are taken into account already when the raw materials base for a new industrial product development is **Salimon et al.**[26] reported that the development and applications of biolubricants are increasing daily due to the strict regulations imposed on mineral oil-based lubricants because of their non-biodegradable wastes. They investigated Plant oils as a potential source of environmentally favorable lubricants because of their biodegradability, renewability, viscosity–temperature relationship, low volatility and excellent lubrication performance. **Findrik et al.**[27] focused on enzymatic esterifications in non-conventional media (organic solvents, ionic liquids, and solvent-free systems) with reference to the water removal. **Muszynski et al.**[28] tested the application of enzyme preparations, such as immobilized lipases from *Candida Antarctica, Pseudomonas cepacia* and *Rhizomucor miehei*, in the synthesis of rapeseed oil fatty acid esters with selected alcohols.

III. MATERIALS AND EXPERIMENTAL SET UP

In the present study of synthesis of biolubricants from the esterification reaction of Oleic acid with i-amyl alcohol by using perchloric acid catalysts following materials are used

1. i-Amyl alcohol
2. Extra pure oleic acid LR CDH
3. Perchloric acid
4. Silica gel self indicating(coarse)LR MERCK
5. Sodium sulphate anhydrous LR CDH

III A-Setup for Esterification Reaction

A photographic view of the set up for esterification reaction is shown in Fig. 1. The whole setup consists A 2000ml 3 neck round bottom flask,. An electric magnetic heater. A magnetic stirrer., Condenser Leibig 250 mm, A thermometer ranges from 0 to 360^{o}C and A tightly fitting stopper.

III-BSetup for Vacuum Distillation:

The setup for vacuum distillation of product mixture is shown in Fig. 3. The photographic view of the above setup of vacuum distillation is shown in Fig..2. This setup consists of the following Round bottom flask socket 1000ml, Borosil a Condenser, leibig 300 mm, cone perfit. , Still head:cone B 24, socket for thermometer B 19, side cone B 24, perfit. Thermometer glass enclosed socket 0-360^{o}C, perfit.A bend with vacuum connection, cone size, perfit. A Heating mental, 300 watt and a 250 ml.

Fig 1: Photographic view of the Experimental Setup for Esterification Reaction

Fig 2: Photographic View of the Setup for Distillation of Product Mixture

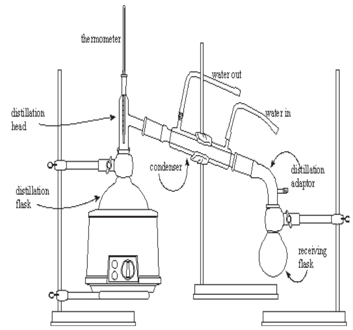

Fig 3 :Setup of Vacuum Distillation

III C-Method The desired amounts of oleic acid and i-amyl alcohol at molar ratio of 1:2 oleic acid/.i-amyl alcohol fraction are introduced in 2000ml three neck flask equipped with a magnetic stirrer, a thermometer and reflux condenser. The mixture was kept in a magnetic heater and stirrer, until it reached the temperature of 70^{o}C. Catalyst perchloric acid (1% with respect to the fatty acid) is then added and the reaction was allowed to occur for two hours at constant temperature. The flask was allowed to cool to room temperature. The mixture was filtered to remove the silica gel from the product. The mixture was then wash repeatedly with distilled water until all the catalyst was removed. Traces of moisture was removed with the help of anhydrous sodium sulphate. Supernatant was decanted and last portion was filtered. The unreacted i-amyl alcohol in the product was distilled over till the temperature reached about 135^{o}C. the product iso amyl oleate was used for testing various lubricating properties.

III D- Characterization of iso amyl oleate Some important specifications of i-amyl oleate ester (base oil) such as flash point, pour point, kinematic viscosity and viscosity index was determined experimentally to its suitability as biolubricant.

Fig 4: Saybolt Viscometer

Fig 5: Cleveland apparatus for flash point

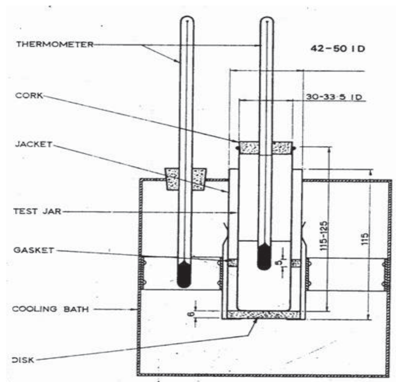

Fig 6 : Pour point set up

III E – Characterisation Results

Experiments have been performed to study esterification reaction between oleic acid and i-amyl alcohol in the presence of perchloric acid Since the esterification reaction is a reversible reaction and produces water, the removal of water from the product mixture during reaction will enhance the conversion. Therefore, esterification reaction in the presence of silica gel has been performed .

$$\underset{\text{Oleic acid}}{C_{18}H_{34}O_2} + \underset{\text{i-Amyl alcohol}}{C_5H_{11}OH} \rightleftharpoons \underset{\text{i-Amyl oleate ester}}{C_{23}H_{44}O_2} + \underset{\text{Water}}{H_2O}$$

Following is the summary of characterization results of i-amyl oleate ester

Catalyst	**Amount of Catalyst**	**Molar Ratios of reactants**	**Rxn. Temp.**	**Flash Point**	**Pour point**	**Kinematic viscosity at 40^{0}C**	**100^{0}C**	**Viscosity Index**
Perchloric acid	1 vol% of Oleic acid	1:2	70^{0}C	194 ^{0}C	< -15^{0}C	13.17	4.03	217.7

Table 1 : Characterization results of iso amyl oleate ester which serves as base oil for Bio Lubricant

IV.CONCLUSION

This study shows that product of esterification reaction of oleic acid and isoamyl alcohol which is iso amyl oleate has very good potential to serve as a base oil for bio lubricant because it has descent characterization results such as flash point in the range of 190-200^{0}C pour point less thn -15 ^{0}C and viscosity index 217.7 more over it is renewable, non toxic , non polluting and cheaper than synthetic oils. Due to growing environmental concerns and depleting crude reserves this can reduce the dependence on mineral oil and other non renewable sources.

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