# SYNTHESIS OF NEEM OIL ESTERS AS BIOLUBRICANT BASE STOCK

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**Abstract-** Global warming has become a worldwide concern, which is highly contributed by the emissions of IC engine combustion products. Inflation in fuel prices as well and shortage of its supply due to unsustainable energy situations world-wide owing to unequal distribution of natural wealth as well as geographical, environmental and economic status are also another concern to look for an alternative source for this. Ever increasing drift of energy consumption is due to over population, transportation and luxurious life style has motivated researches to carry out research on renewable sources as sustainable alternative. In this study renewable, carbon neutral, non-toxic, essentially free of sulphur, bio-lubricants are synthesized as alternative for fossil fuels. Trimethylol propane esters, neopentyl glycol esters, pentaerythritol esters have been developed from Neem oil as lubricant base stocks. The developed base stocks were evaluated for their physico-chemical and lubricant properties. Trimethylol propane esters were prone to be better lubricants compared to other esters synthesized.

Keywords – Calophyllum oil, esters, bio-lubricant.

## I. INTRODUCTION

In present days utilization of crude oil was increased due to increased needs with growing technology and population. Crude oil is non-renewable and biodegradable. Lubricant property in vegetable oils is enhanced by converting them to polyol TMP ester **[1].** The hydraulic fluids based TMP esters of rapeseed oil had good cold stability, friction and wear characteristics, and resistance against oxidation at elevated temperatures **[2].**The production of polyol esters by transesterification of Jatropha oil with methanol and trimethylol propane. The effects of temperature, pressure, ratio of Jatropha oil methyl ester: trimethylol propane and catalyst amount were studied in optimization experiment. **[3].** Preparation of polyol esters based on rapeseed oil, olive oil and lard with neopentyl glycol (NPG) and trimethylol propane (TMP). These polyol esters were characterised with physico chemical properties **[4].** Merja Lämsä, etal., studied on 2-Ethyl-1-hexanol fatty acid esters from rapeseed oil by enzymatic transesterification **[5].**The performance and exhaust emission characteristics of Neem methyl ester with diesel fuel**[6].** Vegetable oil is biodegradable and shows comparable performance as a replacement for mineral oil lubricants **[7].** Vegetable oil-based polyol esters have been produced in various ways from FA **[8,9]** and FAME **[10]**.However, in contrast, Waara et al. [**11]**found that pure synthetic ester (TMP-Oleate and TMP-C8- C10) in a sliding contact resulted in high wear rates and a lot of abrasive marks on the surface. Zulkifli NWM etal **[12]** has studied wear prevention characteristics of a palm oil-based TMP ester as an engine lubricant **[13],** The Kinetics of Transesterification of Palm-based methyl esters with Trimethylol propane. Polyol esters synthesized are eco-friendly and biodegradable which are fire resistance and have good lubricating properties **[14].** Karuna etal., has studied the polyol esters of rubber seed oil as a potential source for hydraulic oils and thumba seed oil as potential bio lubricant base stocks. Polyol esters of 10-undecenoic acid and undecanoic acid are potential lubricant base stock. **[15].** Tamanu based biodiesel used as non conversational fuels in compression ignition engine without any need for modification in engine design **[16].** Tribilogical characteristics of Neem based TMP ester as a better lubricant properties compared to mineral oils. **[17]**in the present study various esters of neem were synthesized and were characterized by NMR, IR and analysed for physico- chemical properties.

**Material & Method**

**Materials:** Neem seeds were collected from GITAM University, Visakhapatnam. TMP (2-ethyl 2-(hydroxyl methyl)-1, 3-propanediol**or** Trimethylol propane), NPG (2, 2-Dimethylpropane-1, 3-diol**or** neopentyl glycol) and PET (2, 2-Bis (hydroxyl methyl) propane-1, 3-diol or pentaerythritol) were purchased from ACRO Organics, India. Aluminium oxide, hexane, toluene and ethyl acetate were purchased from Finar, India. Silica gel was purchased from Fisher Scientifics, Ahmadabad, India. Hydrochloric acid, Sodium thio sulphate and sodium sulphate were purchased from Fisher Scientifics, Mumbai, India. p-TSA (para toluene sulphonic acid) was purchased from AVRA labs, Hyderabad, India. All the above solvents and reagents were of analytical grade and used directly without purification.

**Methods**

**Analytical methods:** The GC analysis was performed with an Agilent 6890 N series gas chromatography equipped with a flame ionization detector. $^{1}H$ NMR spectra were recorded on Avance 300 MHz in $CDCl_3$. Chemical shift values relative to TMS as internal standards were given δ values in ppm. An IR spectrum was obtained on a 1600 FT-IR Perkin -Elmer Spectrometer.

**Physico - chemical properties**: Free fatty acid, density, specific gravity, moisture content, viscosity, flash, fire, cloud, pour and copper strip corrosion were determined using standard ASTM methods. Cloud, pour point, kinetic viscosity bath, copper strip corrosion, flash and fire point apparatus were purchased from Culture Instruments India LLP, Bangalore.

**A typical procedure for the extraction of oil:** The dried, kernels were finely powdered and the oil was soxhlet extracted using hexane as a solvent. The hexane was removed under vacuum and the crude oil (40%) was dried under reduced pressure. The crude oil is used without further purification.

**A typical procedure for the preparation of Neem fatty acid:** Neem oil (300 gm) and aqueous sodium hydroxide solution (54gm in 675 ml water) were stirred mechanically for 4h at 80-90$^{0}$C. The reaction was monitored by TLC using hexane/ethyl acetate (90:10 v/v) solvent system. The reaction was continued until the disappearance of triglyceride in TLC. After completion of the reaction, the reaction mixture was cooled to 50$^{0}$C neutralized with concentrated HCl extracted with ethyl acetate and washed with water. The ethyl acetate layer was dried over anhydrous sodium sulphate and concentrated under vacuum to obtain 270 gm of product. The fatty acid thus obtained were semi solid in nature.

**$^{1}$H NMR ($CDCl_3$, δ ppm):** 0.85 (t,-C$\underline{H}_3$); 1.20-1.24 (m, (-C$\underline{H}_2$-) $_n$); 2.02 (m, CH2-C=C); 2.25 (t,-C$\underline{H}_2$C=O); 5.29 (m, C$\underline{H}$=C$\underline{H}$-).

**IR (neat, $cm^{-1}$)**: 3583 (OH), 3056 (CH=CH), 2859($CH_3$), 1712(C=O).

**A typical procedure for the preparation of Neem neopentyl glycol ester (a):** Neem fatty acids (170gm, 0.6048mol), neopentyl glycol (30 gm, 0.288mol), p-TSA (2 gm based on 1% weight of fatty acid) and 200 ml of toluene were stirred at reflux temperature. The reaction was continued until required quantity of water is been collected in dean stark apparatus and was monitored by TLC using 9:1 hexane and ethyl acetate. After the disappearance of fatty acid the reaction mixture was cooled to room temperature, and toluene was removed under vacuum. Sodium bicarbonate and ethyl acetate solutions were added to the reaction mixture and stirred for half an hour. The organic layer was separated washed twice with water, dried over anhydrous sodium sulphate and concentrated under vacuum. The crude ester was purified by basic alumina column chromatography using 95% of hexane and ethyl acetate as eluent. The product was characterized by $^{1}$HNMR, IR and analyzed for physico chemical properties.

**$^{1}$H NMR ($CDCl_3$, δ ppm):** 0.90 (t,-C$\underline{H}_3$); 1.15-1.4 (m, (-C$\underline{H}_2$-) $_n$); 2.06 (m, CH2-C=C); 2.39 (t,-C$\underline{H}_2$C=O); 4.07 (s, C$\underline{H}_2$-O-C=O); 5.33 (m, C$\underline{H}$=C$\underline{H}$-).

**IR (neat, $cm^{-1}$)**: 2925(-$CH_2$), 2855($CH_3$), 1743(C=O), 1168(COC).

**A typical procedure for the preparation of Neem trimethylol propaneester (b):** Neemfatty acids (270gm, 1.0112mol), Trimethylol propane (43.76gm, 0.3262mol), p-TSA (2.7gm based on 1%

weight of fatty acid) and 250 ml of toluene were stirred at reflux temperature. The reaction was continued until required quantity of water is been collected in dean stark apparatus and it was monitored by TLC using 9:1 hexane: ethyl acetate. After the disappearance of fatty acid the reaction mixture was cooled to room temperature, and toluene was removed under vacuum. Sodium bicarbonate and ethyl acetate solutions were added to the reaction mixture and stirred for half an hour. The organic layer was separated washed twice with water, dried over anhydrous sodium sulphate and concentrated under vacuum. The crude ester was purified by using basic alumina column chromatography using 95% of hexane and ethyl acetate as eluent. The product was characterized by $^1$HNMR,IR and analyzed for physico chemical properties.

**$^1$H NMR ($CDCl_3$, δ ppm):** 0.95 (t,-C$\underline{H}_3$); 1.15-1.4 (m, (-C$\underline{H}_2$-) $_n$); 2.02 (m, CH2-C=C); 2.15-2.2 (t,-C$\underline{H}_2$C=O); 4.0 (s, C$\underline{H}_2$-O-C=O); 5.28 (m, C$\underline{H}$=C$\underline{H}$-).

**IR (neat, cm$^{-1}$):** 3016(-C=C-H); 2926 ($CH_2$), 2854 ($CH_3$), 1735(-C=O); 1216(C-O-C).

**A typical procedure for the preparation of Neem pentaerythritol ester (c):** Neem fatty acids (224 gm, 0.7930mol), pentaerythritol (28 gm, 0.2056mol), p-TSA (2.5gm based on 1% weight of fatty acid) and 220 ml of toluene were stirred at reflux temperature. The reaction was continued until required quantity of water is been collected in dean stark apparatus and was monitored by TLC using 9:1 hexane: ethyl acetate. After the disappearance of fatty acid the reaction mixture was cooled to room temperature, toluene was removed under vacuum. Sodium bicarbonate and ethyl acetate solutions were added to the reaction mixture and stirred for half an hour. The organic layer was separated washed twice with water, dried over anhydrous sodium sulphate and concentrated under vacuum. The crude ester was purified by basic alumina column chromatography using 95% of hexane and ethyl acetate as solvent. The product was characterized by $^1$H NMR, IR and analyzed for physico chemical properties.

**$^1$H NMR ($CDCl_3$, δ ppm):** 0.88 (t,-C$\underline{H}_3$); 1.22-1.41 (m, (-C$\underline{H}_2$-) $_n$); 2.08 (m, CH2-C=C); 2.37 (t,-C$\underline{H}_2$C=O); 4.09 (s, C$\underline{H}_2$-O-C=O); 5.35 (m, C$\underline{H}$=C$\underline{H}$-).

**IR (neat, cm$^{-1}$)**: 2927(-$CH_2$), 2856($CH_3$), 1742(C=O), 1169(COC).

## Results and Discussions

The recompenses of using non edible oils as bio-lubricants compared to mineral oil based lubricants are there easy accessibility in nature, renewability and biodegradability. The existing study is focused on the use of non-edible Neem oil, rich in free fatty acid which is widely available along the coastal areas of India. The seeds of Neem were collected, dried and crushed. The oil was soxhlet extracted using hexane as a solvent. The extracted crude oil is greenish yellow with disagreeable odour and it got darkened during the storage. The physico chemical properties of crude oil were carried out as per ASTM methodsand are tabulated in **Table-1.**

**Table-1:** Physico-chemical properties of Neem oil

| S.no | Properties | Values |
|---|---|---|
| **1** | Color | Greenish yellow |
| **2** | Odour | Disagreeable |
| **3** | Free fatty acid (mg KOH/gm) | 44 |
| **4** | Specific gravity | 0.935 |
| **5** | Flash point ($^0$C) | 185 |
| **6** | Fire point ($^0$C) | 189$^0$C |
| **7** | Viscosity at 40 $^0$C (cSt) | 38.17 |
| **8** | Moisture | 0.35% |
| **9** | Acid number (mg KOH/gm) | 0.23 |
| **10** | Density at 15$^0$C (g/cc) | 0.910 |

Neem seed oil was converted to fatty acid by using aqueous sodium hydroxide solution. The fatty acid composition of the oil is determined by GC and is tabulated in **Table-2.**

**Table 2:** Fatty acid composition of Neem oil.

| | Fatty acids | Compositions |
|---|---|---|
| **1.** | Palmitic (16.0) | 15.23% |
| **2.** | Stearic(18.0) | 15.93% |
| **3.** | Oleic(18:1) | 37.57% |
| **4.** | Linoleic(18:2) | 27.78% |
| **5.** | Others | 3.50 % |

Thefatty acid was esterified with various alcohols such as trimethylol propane, neopentyl glycol and pentaerythritol in presence of p-TSA, refluxed until the required quantity of water is collected in dean stark apparatus and also monitored using TLC. After completion of reaction to the reaction mixture sodium bicarbonate and ethyl acetate were added and the organic was separated and concentrated under vacuum. The crude was purified by column chromatography **(Scheme-1)**. All the esters thus obtained have a pleasant odour, were characterized by $^1$HNMR and IR. The peak at 1735cm$^{-1}$(-C=O) in IR, a triplet at 2.15-2.2 ppm and a singlet at 4.0 ppm in $^1$HNMR confirms the presence of ester.$^1$HNMR and IR Spectra of various esters were given in **Figure-1&2**.

The synthesized esters were evaluated for their physico chemical properties like total acid number, density, colour and evaluated for lubricant properties namely, viscosity, viscosity index (VI), cloud, pour, flash fire point and copper strip corrosion value by using standard ASTM methods. The results were tabulated in table (**Table-3)**.

Density of various esters are in the range of 0.9263 to 1072g/cc. Densities are increasing with increasing alkyl chain by esterification process. This was a good density for lubricant oil.
Kinematic viscosity at 40$^0$C of esters of neopentyl glycol, trimethylol propane and pentaerythritol were 6.8, 8.87 and 9.3 cst respectively. At 100$^0$C the viscosity varied from 1.42 to 3.01cSt. All three polyol esters exhibited high viscosity index more than 200 which is desirable as good lubricant oil.

Pour points of polyol esters of neopentyl glycol, trimethylol propane and pentaerythritol esters are exhibiting -10.1, -16, -13, and -9are respectively. These polyol esters are exhibiting good pour points which are desirable properties for bio lubricants.

All four synthesized polyol esters exhibiting more than 192$^0$C of flash points and more 198$^0$C of fire points. This is an attractive property for lubricant oil. Corrosiveness of the products is found to be very good (1a) for all the four polyol esters.
These properties revealed that the various esters of Neem fatty acids seem to be good feed stock of a various bio lubricant. The present study can support as well as encourage research on using the renewable non-edible oil based bio-lubricants as alternatives.

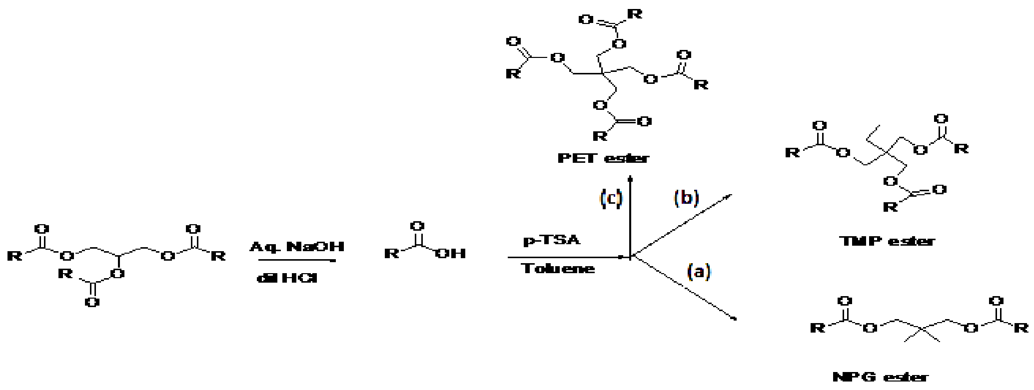
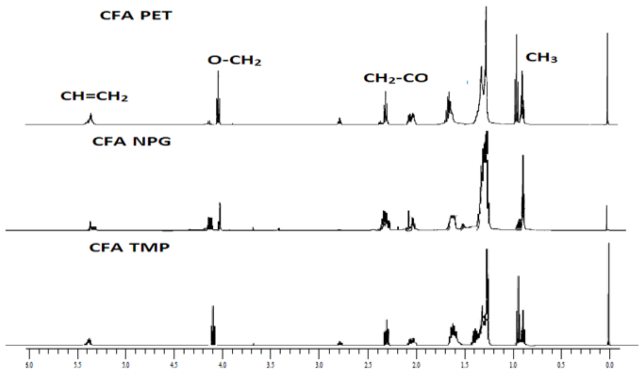



**Table-3:** Physico-chemical and lubricant properties of Neem polyol esters

| .no | Properties | STM method | Trimethylol propane ester | Neopentyl glycol ester | Pentaerythritol ester |
|---|---|---|---|---|---|
| 1 | Colour | - | Transparent | Transparent | Transparent |
| 2 | Odour | - | Fruity | Fruity | Fruity |
| 3 | Moisture | - | 0.1 % | 0.1 % | 0.1 % |
| 4 | Acid number (mgKOH/g) | D1980 | 0.22 | 0.20 | 0.28 |
| 5 | Specific gravity | D4052 | 1.2 | 1.24 | 1.11 |
| 6 | Density at 27$^0$C (g/cc) | D792 | 0.9954 | 0.9623 | 1.064 |
| 7 | Flash point ($^0$C) | D92-01 | 194 | 193 | 192 |
| 8 | Fire point ($^0$C) | D92-01 | 204 | 202 | 198 |
| 9 | Viscosity at 40$^0$C (cSt) | D445 | 8.877 | 6.8 | 12.223 |
| 10 | Viscosity at 100$^0$C (cSt) | D445 | 2.989 | 2.5 | 3.65 |
| 11 | Viscosity index | D2270 | 227 | 248 | 206 |
| **12** | Cloud point ($^0$C) | D2500 | -1.0 | -3.8 | 0.6 |
| **13** | Pour point ($^0$C) | D97 | -13.0 | -16.0 | -9.0 |
| 14 | Coppers strip corrosion | D130 | 1a | 1a | 1a |



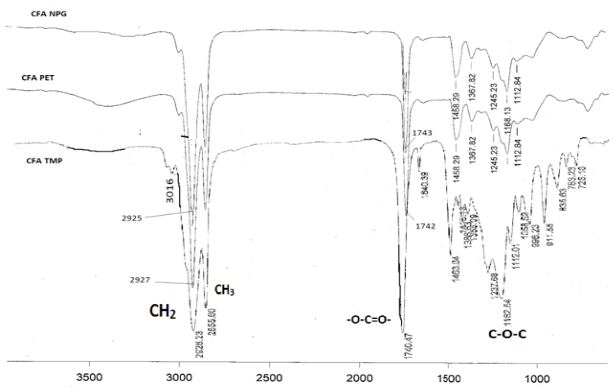




**Figure 1:**[1]H NMR of Neem esters of trimethylol propane, neopentyl glycol and pentaerythritol esters respectively.

**Figure 2:** IR of Neem neopentyl glycol, pentaerythritol and trimethylol propane esters respectively.

## Conclusion

The bio lubricant production from Neem oil using various alcohols has potential to replace the petroleum based lubricants. Non edible vegetable oils shows potential supply of bio lubricants owing to the physicochemical properties which are comparable to petroleum based lubricants. The synthesized various esters are environmental friendly less toxic and are from renewable resources..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