

PART-3/CHAPTER-3

PERFORMANCE EVALUATION OF CHEMICALLY MODIFIED VEGETABLE OILS TOWARDS THE DEVELOPMENT OF BIODEGRADABLE GREENER LUBRICANT BASE STOCK

3.3.1 INTRODUCTION

Environment-friendly biodegradable lubricants, based on plant oil could replace or partially substitute conventional mineral oil is a big challenge. They have excellent rheological properties. (Vegetable oils have high viscosity index (above 200) high flash point as well. Despite having huge advantages and being biodegradable and environment friendly, vegetable oils suffer from some inherent limitations mainly low thermo-oxidative stability due to the presence of polyunsaturation [6]. Hence untreated vegetable oils cannot be used directly as a lubricant. However, this problem can be solved by some chemical modifications such as transesterification, epoxidation, selective hydrogenation, polymerization, etc. High contents of unsaturated fatty acid in most vegetable oils can be converted into epoxy fatty acid by conventional epoxidation, [11]. Epoxidized vegetable oil can act as a raw material for the synthesis of a variety of chemicals including polyols, glycol, carbonyl compound, lubricants, plasticizers for polymer, etc. because of the high reactivity of oxirane ring [7]. Castor oil is obtained from castor seeds which are available in nature. It contains a high percentage of triacylglycerol of ricinoleic acid (85–95%) which is a C–18 fatty acid having a double bond at C–9 and a hydroxyl group at C–12. Due to the trifunctional nature of castor oil, it can be used as a monomer for the preparation of lube oil polymeric additives as well as base stock

with multifunctional properties. Castor oil contains hydroxyl monounsaturated triglycerides which via hydrogen bonding raises the viscosity to a very good level. Castor oil has higher viscosity index compared to super-refined mineral oils [8]. In our earlier work, castor oil was explored towards the synthesis of multifunctional greener additives for lubricating oil[9]. Soyabean oil, one of the most abundant and inexpensive renewable sources towards the formulation of high molecular weight polymers, consists of polyunsaturated fatty acids with the main component being linoleic acid (50% w/w) [10]. Hong–Sik Hwang, Sevim Z. Erhan studied the properties of synthetic lubricant base stocks from epoxidized soybean oil and Guerbet alcohols [11]. Linseed oil is also another potential candidate in this field in which the level of unsaturation for the triglyceride is somewhat greater than that for soybean oil [12] In our previous work linseed oil-based biodegradable homo and copolymers were prepared towards the development of multifunctional greener additives for lube oil[13]. Olive oil is also a potential candidate in the lubricant industry as it is commercially available, cheap, and contains about 86 % of total active unsaturation. P. Ghosh et al. have conducted several studies on sunflower oil-based lubricants and additives which accounted for its vast application in the lubricant industry[14-16]. Due to high viscosity index and low pour point, these vegetable oils can be treated as a source of potential lube base stock. Lack of Thermal stability due to the unsaturation present in the triglyceride moiety is the main reason that they cannot be used directly as lube. In this context, we made epoxides of vegetable oils followed by epoxy ring-opening by different alcohols and studied their properties to determine whether they can be treated as alternate lubricant base stock. The main constituents of vegetable oils are triglycerides (95–97%). The general structure of triglyceride found in most of the vegetable oils is

shown in Figure 3.3.7.1. In our present study Vegetable oils like linseed oil (LO), castor oil (CO), olive oil (OLO), soybean oil (SBO), and sunflower oil (SFO) were epoxidized and characterized by FTIR and NMR spectroscopy. The reaction of epoxidized linseed oil with 2-ethyl hexanol, dodecanol, n-octanol, 1-decanol, and isodecanol in the presence of a catalytic amount of H₂SO₄ provided ring-opened products. These ring-opened products of linseed oil exhibited better low-temperature flow i.e. better pour point (PP) and high viscosity index (VI). Ring opened products with isodecanol and 2 ethyl hexanol showed better results compared to others. CO, OLO, SBO, SFO epoxide rings were also opened through the same procedure using isodecanol and the products exhibited high viscosity index and excellent low-temperature flow as well. Ring opened products displayed better thermal stability when passed through thermogravimetric analysis (TGA) compared to the mineral base oil. Better pour point, high viscosity index value, thermo oxidative stability, and better antiwear (AW) property make these products an environmentally benign alternative to mineral lubricating oil. The presence of unsaturated fatty acids like oleic, linoleic, linolenic, etc and saturated fatty acids like tetradecanoic, palmitic, stearic has been responsible for its versatile applications such as in-wall finishes[1], paints[2], electrodeposition paints [3], water thinnable primers[4], and printing inks [5], etc.

3.3.2 EXPERIMENTAL

3.3.2.1 MATERIAL USED

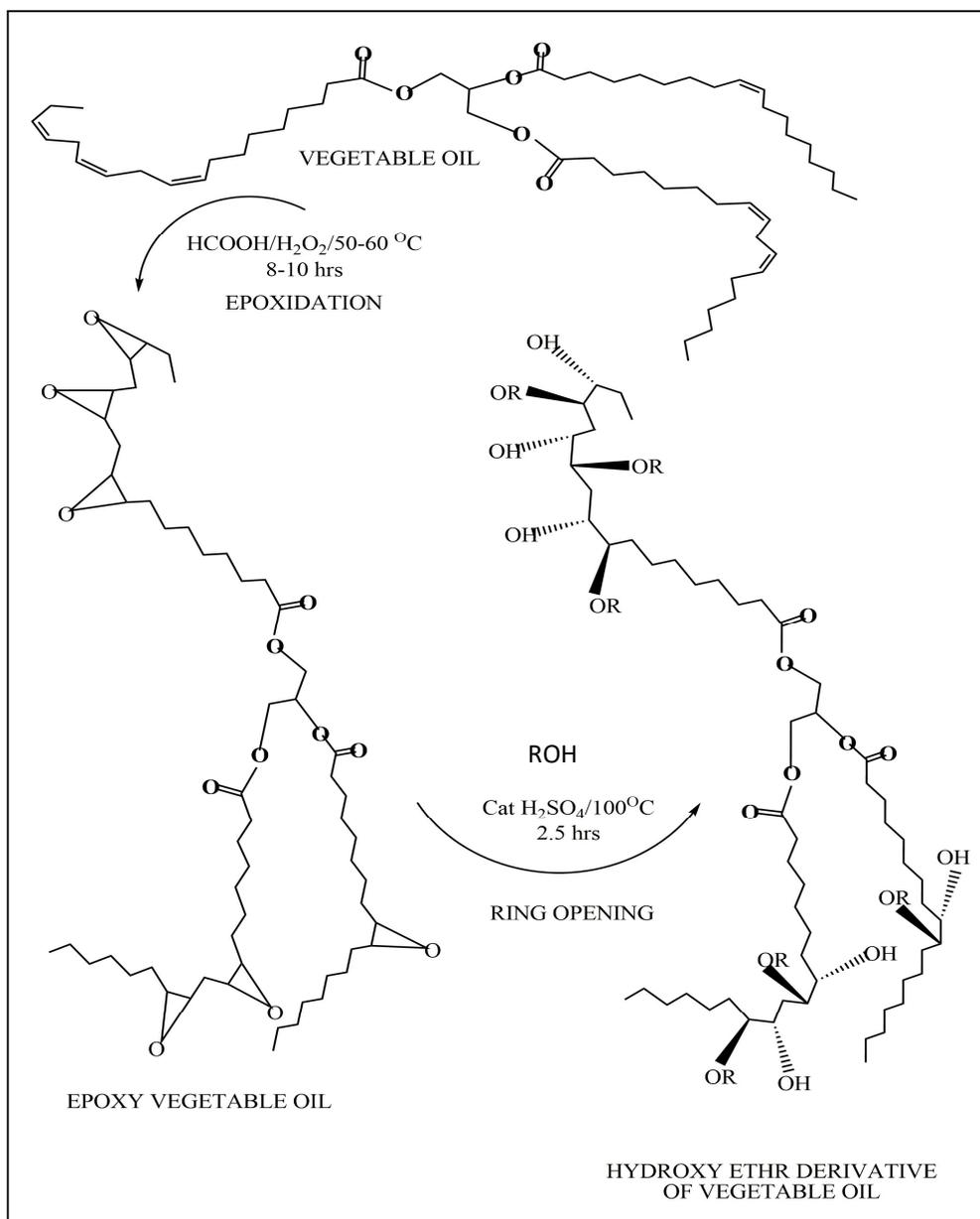
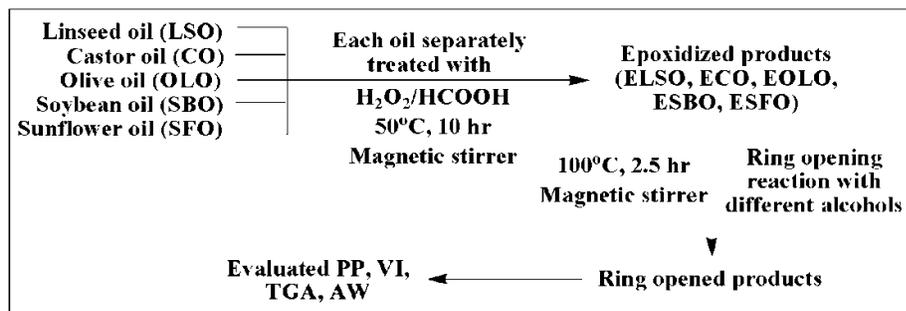
Linseed oil, castor oil, olive oil, sunflower oil, and soybean oil were brought from a local market and used directly. The physical properties of the vegetable oils and the mineral base oils are given in Table:- 3.3.7.1. The fatty acid composition of the vegetable oils is given in Table:- 3.3.7.2 H₂O₂ (30%) used at it was bought from

MERCK. Formic acid (98% Thomas Baker Pvt Ltd Ind), Concentrated H₂SO₄ (98% MERCK), 2-ethyl hexanol (99%Sigma Aldrich), dodecanol (99% Sigma Aldrich), n-octanol (99% LOBA Chemicals Pvt Ltd Ind), 1-decanol (99%Sigma Aldrich), isodecanol (99% LOBA chemical Pvt Ltd Ind) were used after distillation.

3.3.2.2 VEGETABLE OIL EPOXIDATION AND ITS PURIFICATION

At first, linseed oil and formic acid (1.0: 0.4 molar ratio) were mixed in a 2 neck RB fitted with a condenser & set over a water bath at a temperature of 50⁰C and speed of 550 RPM on a magnetic stirrer. The mixture was stirred for 10 min. To start the epoxidation, hydrogen peroxide (30 %) was gradually changed into the mixture during the first 5 hr of reaction in the molar ratio of 1: 1.7 concerning the oil and peroxide[11]. After charging of H₂O₂ was completed, the reaction continued by mixing and controlling the temperature at 50⁰ C for a further 5 hr. After that, the mixture was cooled down and neutralized by water. Diethyl ether was used to enhance the separation of the oil production from the water phase. The final product was dried out by heating less than 50⁰C. Three replications were performed concurrently. Similarly, castor oil epoxide and epoxide of other vegetable oils were prepared[11]. Epoxides have active sites and are further treated with different sets of chemicals to obtain end products with the diversified application. The epoxides were characterized by FTIR and NMR spectra and used for the next step.

Scheme 3.3.1:-Preparation of epoxy vegetable oil and subsequent ring-opening



3.3.2.3 RING-OPENING REACTION OF VEGETABLE OIL EPOXIDE

A mixture of epoxidized linseed oil (ELSO) and 2-ethyl hexanol (1:5 molar ratio of epoxide and alcohols) was heated at 90°C with stirring. Sulfuric acid (2%) was added dropwise and the mixture was stirred at 100°C for 2.5 hr. When the reaction mixture turned brownish, it was cooled by adding ice and saturated aqueous sodium bicarbonate. It was extracted with ethyl acetate, dried over anhydrous Na₂SO₄. The remaining solvent was evaporated under vacuum at 80°C to have the ring-opened product [11]. Similar reactions were carried out using dodecanol, n-octanol, 1-decanol, and isodecanol under the same reaction condition stated above. Castor oil epoxide (ECO), olive oil epoxide (EOLO), soybean oil epoxide (ESBO), sunflower oil epoxide (ESFO) was treated with isodecanol in 1: 2.5 molar ratio of epoxide and alcohol under the same reaction condition to have the ring-opened products. The ring-opening reaction was monitored by the disappearance of epoxy ring hydrogen.

3.3.3 MEASUREMENTS

3.3.3.1 INSTRUMENTATION

- **SPECTROSCOPIC MEASUREMENTS**

IR spectra of the vegetable oil epoxides were recorded on a Shimadzu FT-IR 8300 spectrometer using 0.1mm KBr cells at room temperature within the wavenumber range of 400 to 4000 cm⁻¹. NMR spectra were recorded in Bruker Avance 300 MHz FT-NMR spectrometer using a 5 mm BBO probe in CDCl₃ solvent and tetramethylsilane (TMS) was used as reference material.

- **THERMOGRAVIMETRIC ANALYSIS (TGA)**

TGA data were recorded on Shimadzu TGA-50 system, at a heating rate of 10° C/min. Results are summarised in Table:- 3.3.7.3. The uncertainty in determining percent weight loss (PWL) within the range was $\pm 1.2\%$.

3.3.3.2 PERFORMANCE EVALUATION

- **PERFORMANCE EVALUATION - POUR POINT**

The pour point of the ring-opened products was measured according to the ASTM D 97-09 [18] method using cloud and pour point tester model WIL-471 (India) and a comparison was carried out against base oil. The pour point data are given in Table:- 3.3.7. 4.

- **PERFORMANCE EVALUATION - VISCOSITY INDEX**

Viscosity index (VI) is the change of viscosity with temperature and is a unitless parameter. The higher the value of VI, the smaller is the change of viscosity at high temperature. It was calculated according to ASTM D 2270-10 [17]. The kinematic viscosities of the lubricant composition were determined at 40°C and 100°C which are essential to calculate the VI. A comparison of VI data between the ring-opening products of ELSO and ECO with base oil is listed in Table:- 3.3.7.5.

- **PERFORMANCE EVALUATION - ANTIWEAR TEST**

The antiwear performance of the ring-opened products was evaluated by Four-ball Wear Test apparatus (FBWT) following the ASTM D 4172-94 [19] method. In this experiment, the wear scar diameter (WSD), a parameter for the determination of antiwear (AW) performance of the oils, has been measured applying weld load of 392 N (40 Kg) at 75°C for 60 min. The results are tabulated in Table:- 3.3.7.6.

3.3.4 RESULT AND DISCUSSION

3.3.4.1 SPECTROSCOPIC ANALYSIS

Spectral data of all the vegetable oils give an almost similar result. IR absorption band around 1745 cm^{-1} corresponds to the C=O stretching in the ester carbonyl group in triglyceride moiety in vegetable oil, a broad peak at 3437.95 cm^{-1} corresponds to the –OH group present in the castor oil (ricinoleic acid). Epoxidized vegetable oils produce a new absorption around 822 cm^{-1} and 845 cm^{-1} which indicate the presence of an epoxy ring. The ring-opened products have absorption ranging from 1738 cm^{-1} to 1740 cm^{-1} (Figure:-3.3.7.3 for ELSO) corresponding to the ester C=O group in the ring-opened epoxidized vegetable oils. Broad absorption ranging from 3420 cm^{-1} to 3450 cm^{-1} corresponds to the –OH group in the ring-opened product. Completion of the ring-opening reaction was confirmed by checking the disappearance of epoxy signals at 1158 , 845 , and 822 cm^{-1} in the IR spectrum (Figure:- 3.3.7.8 for ELSO+isodecanol).

The ^1H NMR data of the epoxidized vegetable oils exhibited the presence of secondary and primary glycerol proton at δ 5.10–5.20 ppm and 4.10–4.30 ppm, respectively. The proton signal centered at δ 3.00 ppm is evident for the presence of epoxy protons. This is further substantiated by the disappearance of the olefinic proton signals in the region between δ 5.34–5.43 ppm. The broad intense signal observed in the region δ 1.26–1.63 ppm is due to the presence of many methylene protons. Furthermore, the proton signal at δ 0.89 ppm is characteristic of terminal methyl groups. Ring-Opening product of the epoxides of linseed oil, castor oil, olive oil, soybean oil, and sunflower oil with isodecanol exhibited a similar appearance in NMR spectra. In the ring-opened products, peaks around δ 3.00 ppm corresponding to epoxy protons are absent.

The ^{13}C NMR data also indicated the presence of the carbonyl carbon (O=C) at δ 173.06 ppm, glycerol (CH) at δ 68.95ppm, and glycerol (CH₂) at δ 62.04–64.99ppm, methylene carbons (CH₂) at δ 22.64–34.03 ppm, and methyl carbon (CH₃) at δ 14.06 ppm. On inspection of the ^{13}C NMR spectrum of linseed oil, there are diagnostic signals in the region δ 120–130 ppm which accounted for the olefinic carbons. These signals were not detected in the epoxidized linseed oil which justifies the disappearance of the double bonds and formation of epoxides. This is further supported by the observed increase in the intensity of the epoxy carbon. Furthermore, the triglyceride structure remained intact after epoxidation. Other vegetable oils also produced similar peaks.

3.3.4.2 ANALYSIS OF THERMAL STABILITY

TGA data (Table:- 3.3.7.3) supported that the prepared products were thermally more stable than the mineral base oil. A lower PWL value indicates higher thermal stability. It is found that the percentage of degradation of the ring-opened products of the vegetable oil epoxides at a particular temperature is lower compared to the mineral base oil. This observation simply implies that chemically modified vegetable oils are far resistant against thermal degradation than the mineral base oil under consideration. At 473 K mineral base oil degrades almost completely (PWL 98) whereas the chemically modified vegetable oils degrade almost completely (PWL around 90) above 600K. From this point of view, these chemically modified vegetable oils are more reliable as lubricant base stock.

3.3.4.3 ANALYSIS OF POUR POINT DATA

From Table:- 3.3.7.4 data it is observed that the ring-opening product of ELSO with 2 ethyl hexanol, isodecanol; and ECO, EOLO, ESBO, ESFO with isodecanol exhibited better low-temperature flow. This may be attributed to the

morphology of the branched alcohol moiety that hinders the formation of the wax crystal network. This result implies that at lower temperatures these chemically modified vegetable oils are easier to handle than the mineral base oil.

3.3.4.4 ANALYSIS OF VISCOSITY INDEX DATA

Viscosity may be the most important parameter for lube oil. Vegetable oil has fare viscosity index (Table:- 3.3.7.1) but due to the low thermal-oxidative stability, it can't be directly used as a lubricant. After modification of vegetable oils, they can be considered for comparison with mineral oil. Table:- 3.3.7.5 indicates the possibility of using them as lube base stock. These data sought for the utilization of chemically modified vegetable oils over a broad temperature range since they can sustain their viscosity at an elevated temperature quite well.

3.3.4.5 ANALYSIS OF ANTIWEAR PERFORMANCE DATA

The tribological properties of the lubricant compositions at different mass fractions were determined by measuring WSD values through the FBWT apparatus. By analyzing Table:- 3.3.7.6 data it is evident that the modified vegetable oils produce less wear in engine condition. The chemically modified vegetable oils strengthen the film through chemical and physical bonding between polar functional groups and metal atoms on the metallic surface. Due to the presence of long polar fatty ester chains of these oils showed better AW property compared to the mineral base oil. Due to polar -OH groups, the ring-opened products form comparatively stronger bonds with metal atoms and exhibit better AW property. Among all the chemically modified vegetable oils under consideration, a ring-opened product of castor oil epoxide exhibited the best result in terms of antiwear performance.

3.3.5 CONCLUSION

Epoxidation followed by ring-opening reaction with suitable alcohols has provided an efficient easy route towards the formation of vegetable oil-based biodegradable and thermally stable lubricant base stock with the better low-temperature flow, viscometric properties, and antiwear performance. These chemically modified vegetable oils can be used directly or in a mixture with mineral base lube for better performance. The above study accounts for the replacement of toxic mineral base oil with environment-friendly, biodegradable greener vegetable oil-based products as lubricant base stock.

ACKNOWLEDGMENT

Thanks to UGC, and the University of North Bengal for providing me the opportunity. Thanks to IOCL, Dhakuriya West Bengal for providing Base Oil.

3.3.6 REFERENCES

References are given in BIBLIOGRAPHY under “**Chapter-3 of Part-3**”.

3.3.7 TABLES AND FIGURES

FIGURE 3.3.7.1

GENERAL STRUCTURE OF TRIGLYCERIDE FOUND IN VEGETABLE OIL.

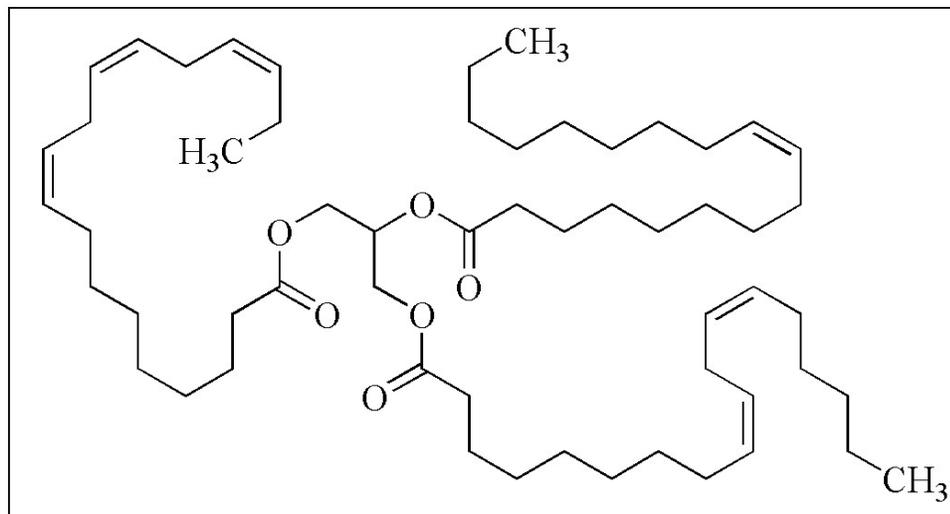


TABLE 3.3.7.1

PHYSICAL PROPERTIES OF BASE OIL (BO), LINSEED OIL (LSO), CASTOR OIL (CO), OLIVE OIL (OLO), SOYBEAN OIL (SBO), SUNFLOWER OIL (SFO)[20]

Physical properties	BO*	LSO	CO	OLO	SBO	SFO
Density (gcm^{-3} at 25°C)	0.95	0.93	0.88	0.92	0.86	0.91
Viscosity at 40°C in cSt	24.211	15.22	173	41.7	28	33.8
Viscosity at 100°C in cSt	4.47	6.33	15	8.8	7.55	8.1
Pour Point (PP in $^{\circ}\text{C}$)	-6	-21	-27	-2	-9	-17
Flash Point ($^{\circ}\text{C}$)	225	>280	200	316	252	245

*BO collected from IOCL, Dhakuria, West Bengal

TABLE 3.3.7.2

FATTY ACID (IN %) COMPOSITION OF VEGETABLE OILS [20]

Vegetabl oil	Palmitic acid (16:0)	Stearic acid (18:0)	Oleic acid (18:1)	Ricinoleic acid (18:1)	Linoleic acid (18:2)	Linolenic acid (18:3)
Olive	14	2	64	–	16	2
Castor	3	3	9	75	10	–
Soybean	6	5.2	20.2	–	63.7	5
Linseed	5	4	19.1	–	15.3	56.6
sunflower	6.1	5.3	21.4	–	66.4	–

TABLE 3.3.7.3

TGA DATA OF THE MODIFIED VEGETABLE OILS IN COMPARISON TO THE BASE OIL

Sample	Decomposition temperature (K)	Percent weight loss (PWL)
Base Oil	393/473	38/98
ELSO + 2-Ethyl hexanol	451/573	15/90
ELSO + Dodecanol	453/571	14/93
ELSO + n-Octanol	468/608	15/92
ELSO + 1-Decanol	470/610	15/96
ELSO + Isodecanol	483/613	13/91
ECO + Isodecanol	483/603	21/95
EOLO + Isodecanol	473/613	14/92
ESBO + Isodecanol	453/598	18/96
ESFO + Isodecanol	462/593	14/91

TABLE 3.3.7.4

POUR POINT DATA OF MODIFIED VEGETABLE OILS IN COMPARISON TO BASE OIL AND GRAPHICAL REPRESENTATION.

Sample	Pour point in °C
Base Oil	-6
ELSO + 2-Ethyl hexanol	-15
ELSO + Dodecanol	-2
ELSO + n-Octanol	-7.2
ELSO + 1-Decanol	-3.6
ELSO + Isodecanol	-18.4
ECO + Isodecanol	-22
EOLO + Isodecanol	-19.4
ESBO + Isodecanol	-18
ESFO + Isodecanol	-17

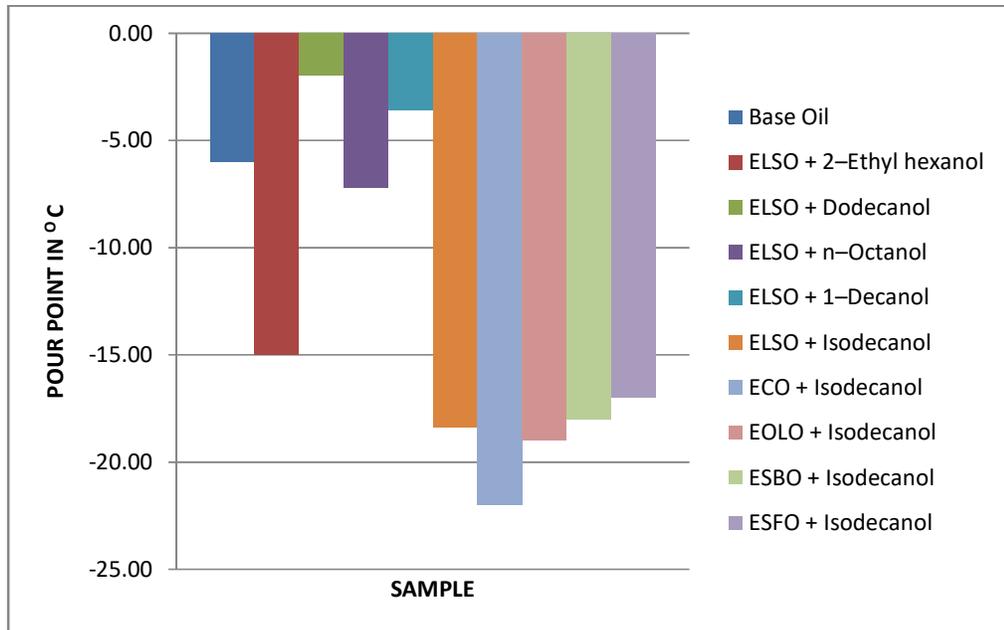


TABLE 3.3.7.5

VISCOSITY INDEX DATA OF MODIFIED VEGETABLE OILS IN COMPARISON TO BASE OIL AND GRAPHICAL REPRESENTATION.

Sample	Viscosity index
Base Oil	89.87
ELSO + 2-Ethyl hexanol	248
ELSO + Dodecanol	256
ELSO + n-Octanol	238
ELSO + 1-Decanol	259
ELSO + Isodecanol	264
ECO + Isodecanol	138
EOLO + Isodecanol	154
ESBO + Isodecanol	268
ESFO + Isodecanol	207

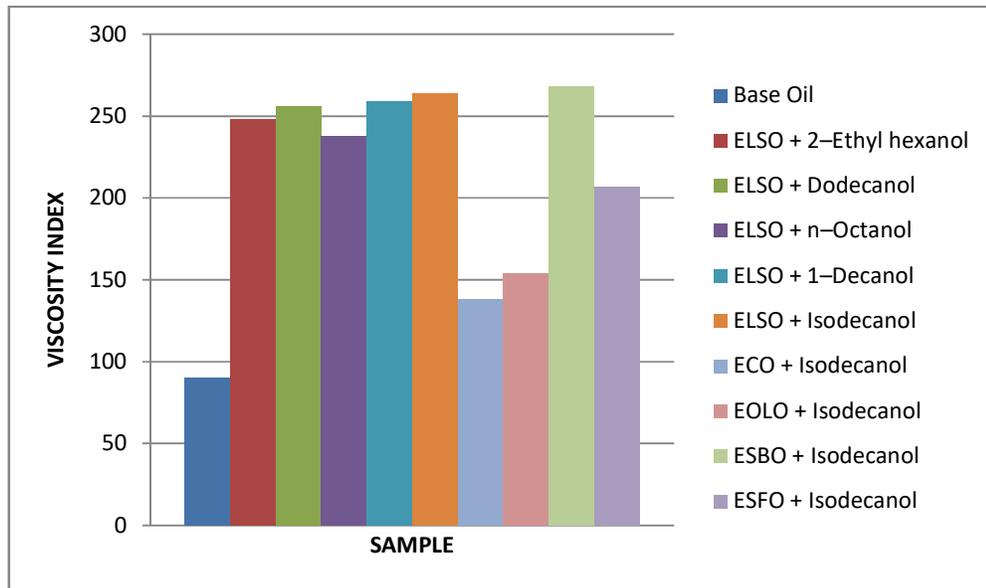


TABLE 3.3.7.6

WEAR SCAR DIAMETER (WSD) VALUES OF THE MODIFIED VEGETABLE OILS IN COMPARISON TO THE BASE OIL AND GRAPHICAL REPRESENTATION.

Sample	WSD x 10 ⁻³ (m)
Base Oil	1.119
ELSO + 2-Ethyl hexanol	0.868
ELSO + Dodecanol	0.835
ELSO + n-Octanol	0.856
ELSO + 1-Decanol	0.882
ELSO + Isodecanol	0.868
ECO + Isodecanol	0.616
EOLO + Isodecanol	0.989
ESBO + Isodecanol	0.776
ESFO + Isodecanol	0.798

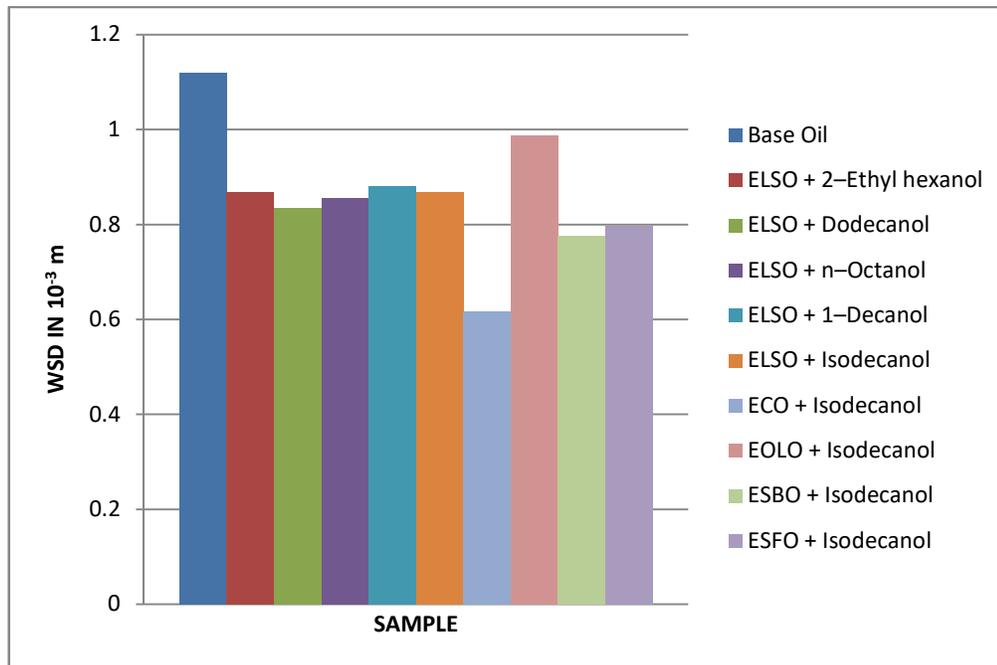


FIGURE 3.3.7.2

FT IR SPECTRA OF LINSEED OIL (LSO)

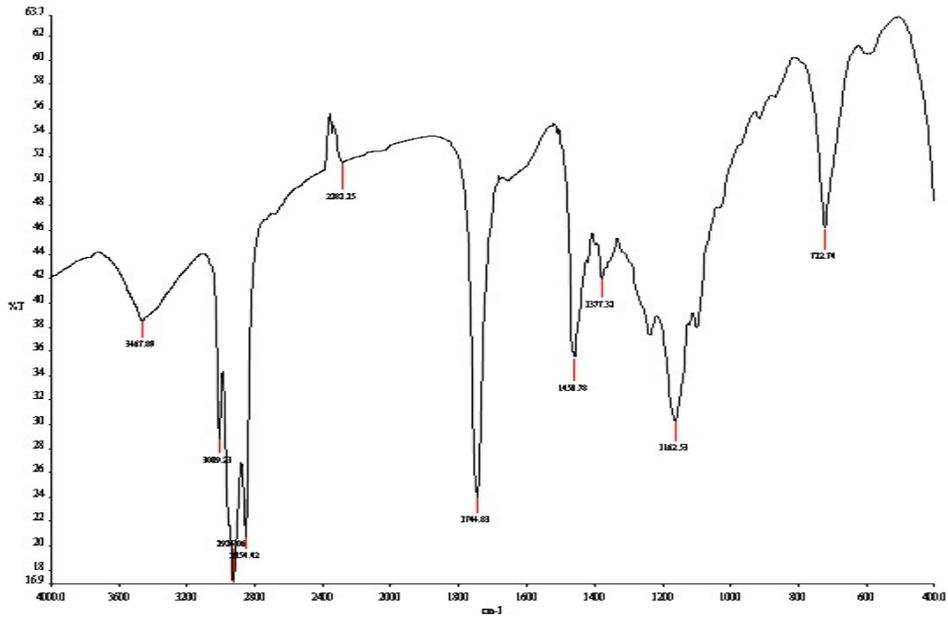


FIGURE 3.3.7.3

FT IR SPECTRA OF EPOXY LINSEED OIL (ELSO)

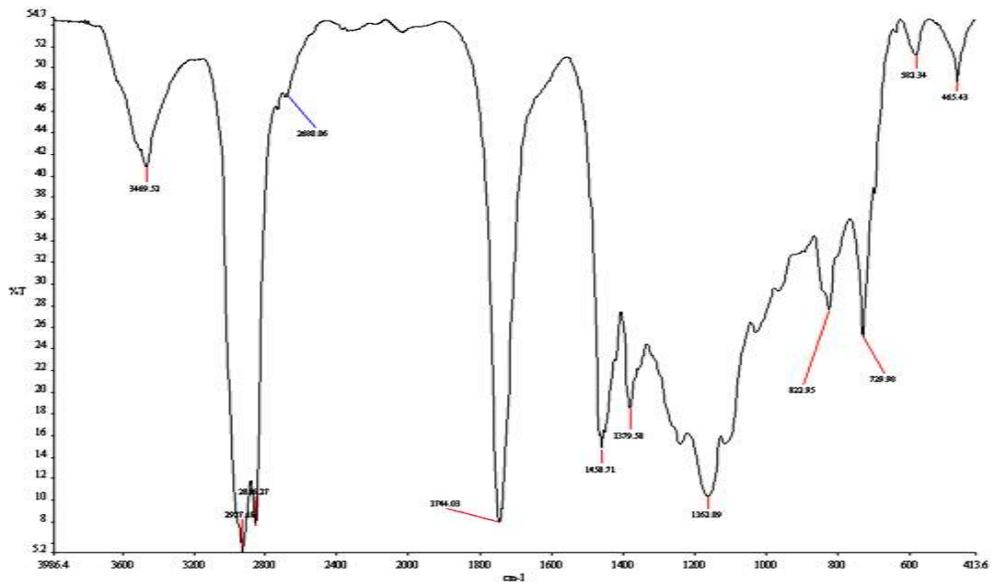


FIGURE 3.3.7.4

FT IR SPECTRA OF ELSO+2ETHYLHEXANOL

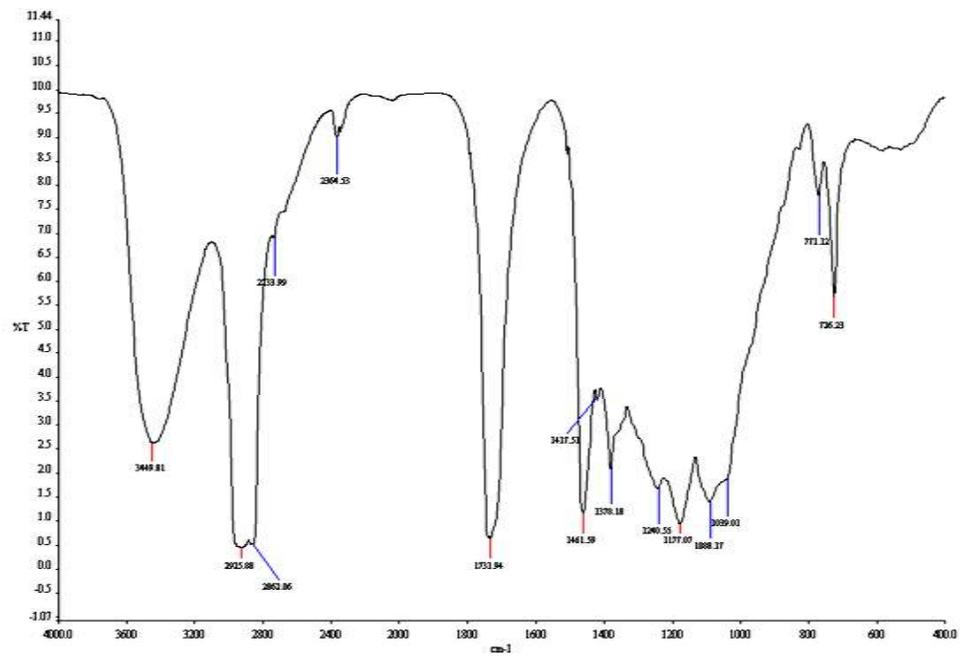


FIGURE 3.3.7.5

FT IR SPECTRA OF ELSO+DODECANOL

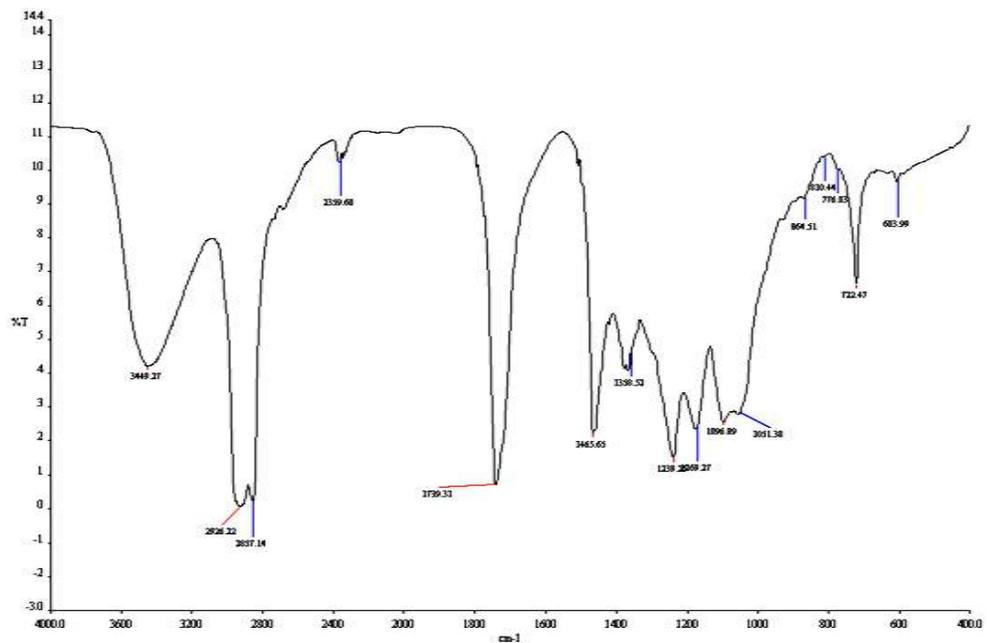


FIGURE 3.3.7.8

FT IR SPECTRA OF ELSO+ISODECANOL

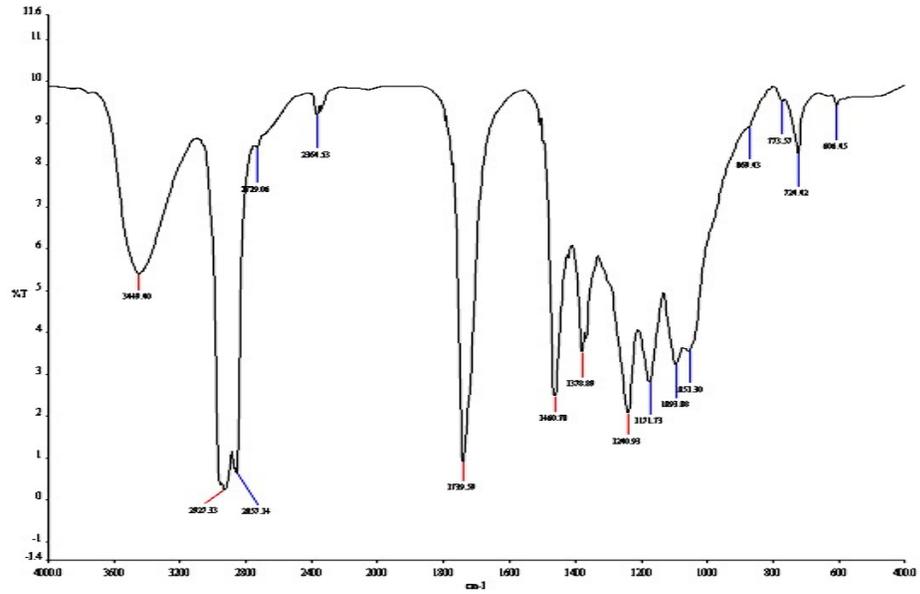


FIGURE 3.3.7.9

FT IR SPECTRA OF ECO+ISODECANOL

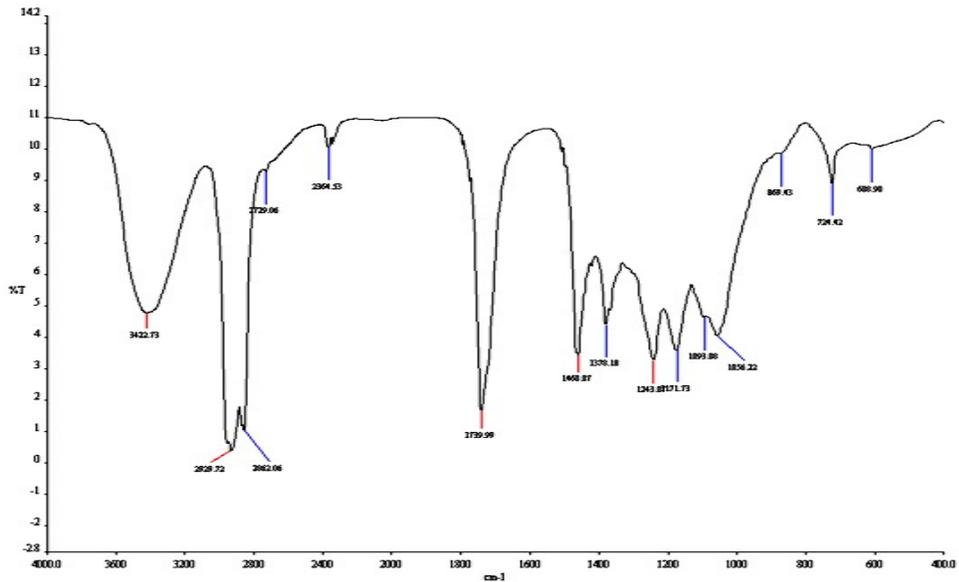


FIGURE 3.3.7.10

FT IR SPECTRA OF EOLO+ISODECANOL

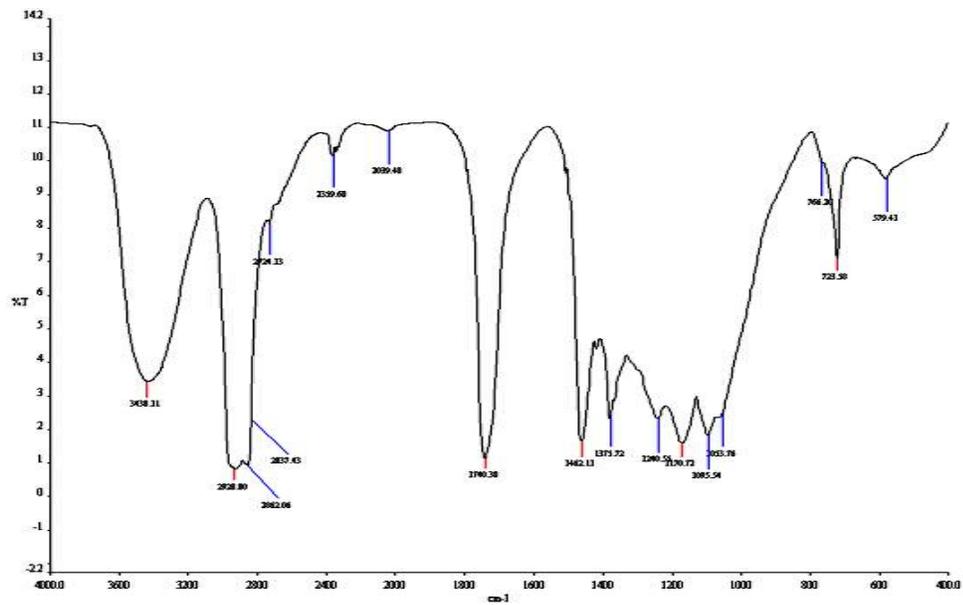


FIGURE 3.3.7.11

FT- IR SPECTRA OF ESBO+ISODECANOL

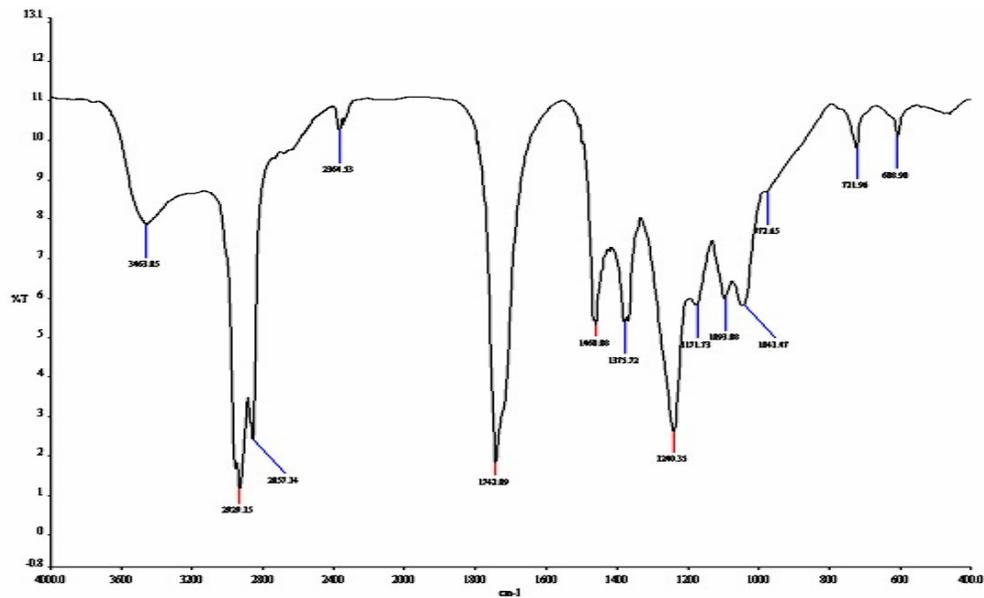


FIGURE 3.3.7.12

FT IR SPECTRA OF ESFO+ISODECANOL

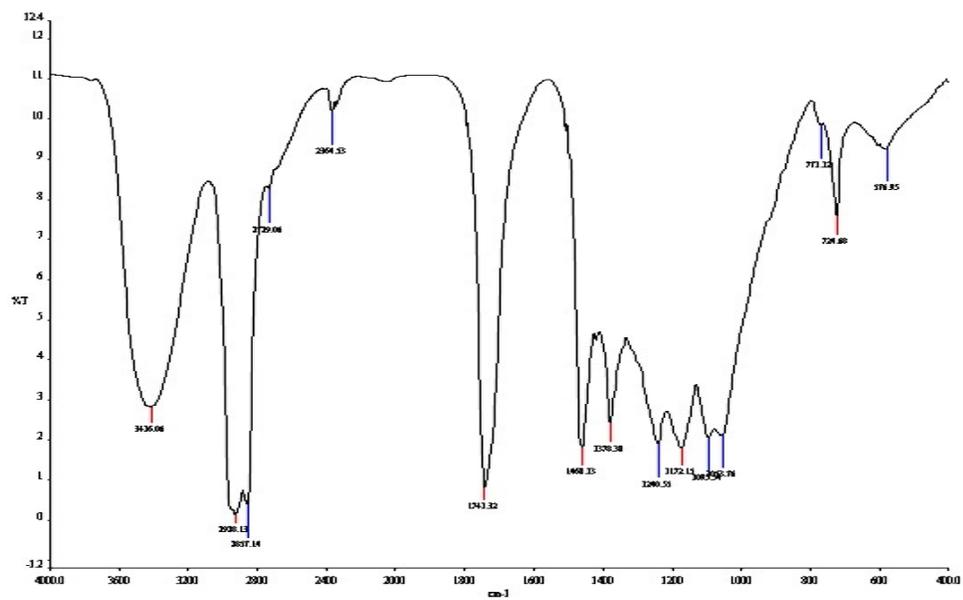


FIGURE 3.3.7.13

REPRESENTATIVE ^1H NMR SPECTRA OF (A)LSO,(B) ELSO

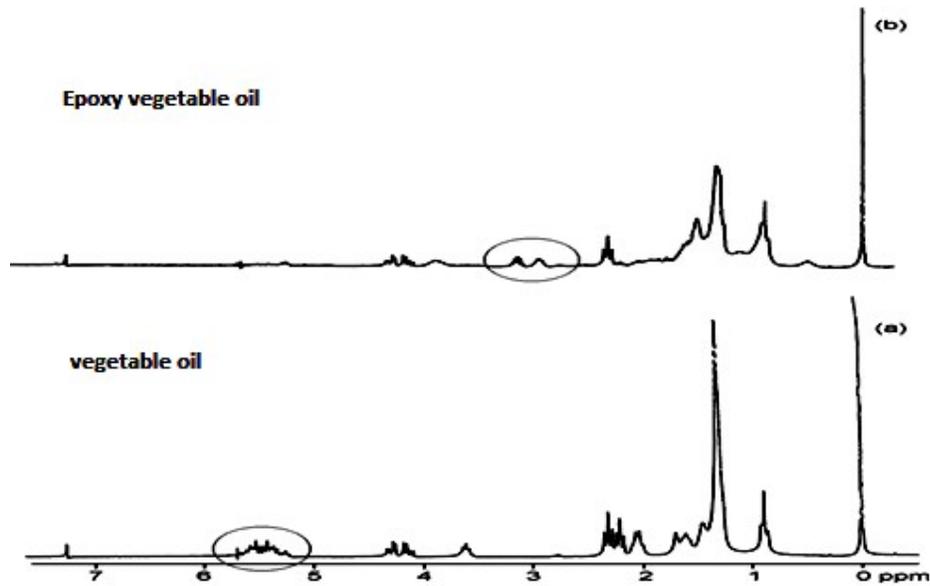


FIGURE 3.3.7.14

REPRESENTATIVE ^1H NMR SPECTRA OF ELSO+ ISODECANOL

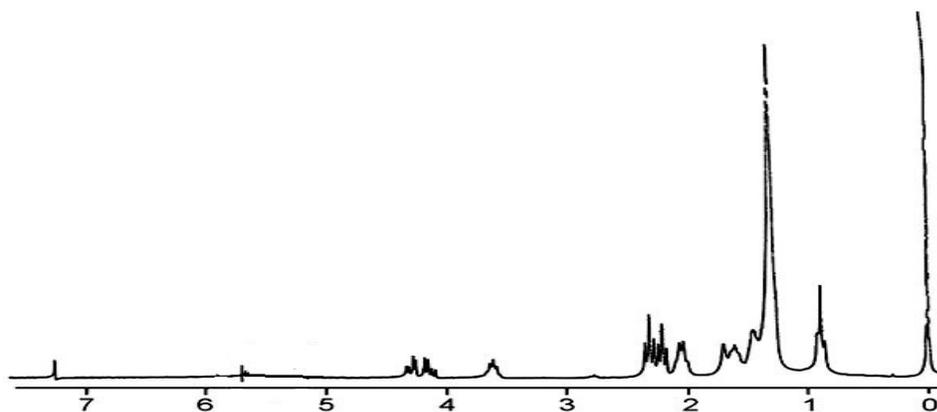


FIGURE 3.3.7.15

^{13}C NMR SPECTRA OF LSO

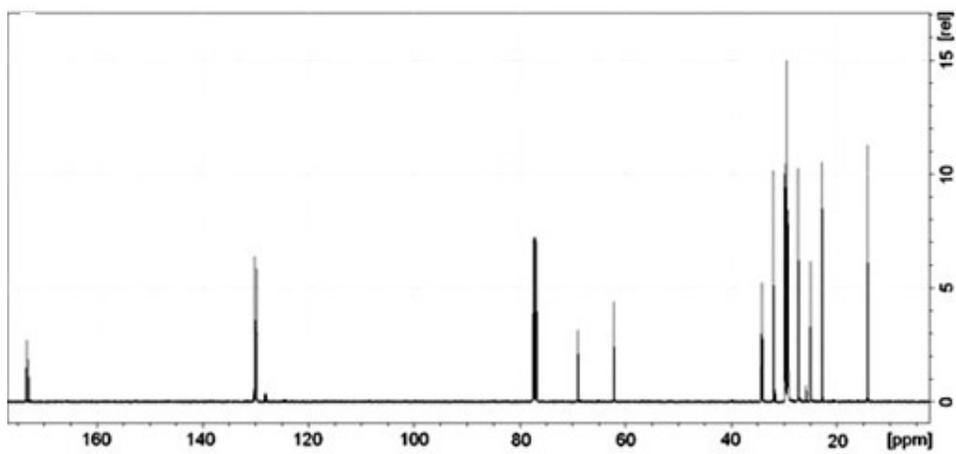


FIGURE 3.3.7.16

^{13}C NMR SPECTRA OF ELSO

