Novelty Journals

ISSN 2394-9716

International Journal of Novel Research in Interdisciplinary Studies
Vol. 2, Issue 4, pp: (1-7), Month: July - August 2015, Available at: www.noveltyjournals.com

Comparative Study –A Mineral Oil Based Lubricant and Lubricant Obtained From Vegetable Oil

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***Abstract*: Word petroleum is better recognized by the crude obtained through PETRA(Greek ROCK), the chemical nomenclature of oil generally is of CnH2n+2(alkane) type,ofwhich petrol comes in the range of C5 to C8,diesel C9 to C16 and fuel oil and lubricating oil C>16.in its refined form. The thermal properties of lubricating oil obtained from hydrocarbons are not said to be environment friendly or ecofriendly due to the production of several irritative substances known as toxins and are said to be responsible for causing eye, ear and throat inflammation along with several type of allergies when they are released in to atmosphere. Besides that the thermal properties of lubricating oil obtained from vegetables are not so much toxic, harmful and accidentally disasterous.It has been found that the obtainable lubricating oil is far more ecofriendly or environment friendly and equally biodegradable comparatively. Because the vegetable based lubricating oil remains less oxidative, therefore causes a minute disadvantage in comparison to the mineral oil. The present paper discusses, describes and highlights some of the necessary and essential properties which are meant for a lubricating oil to be good and most suitable for proper functioning of a engine.**

***Note:* Spectral Analysis, Viscosity and Viscosity Index highlight the physico-chemical properties and biodegra dation in aerobic condition reflects the edaphic and environmental properties of oil.**

***Keywords:* Green Chemistry, Tribology, Biodegradation, Lubricants.**

1. INTRODUCTION

It has been observed that approximately 50% of all lubricants which is sold worldwide gets released in to the environment through total loss applications such as volatility, spillage and accidents. E.U.and U.S.together reports the loss of $2.3*10^9$ L of lubricants in year 1990.(Schneider 2006;Salimon at al 2010;Horner 2002).

Such environmental cause and loss enforce strictly the adoption and thereafter use of the following upgraded brands of lubricants in industry, forestry, agriculture, water treatment equipments such as European Ecolabel (Mang and Dresel 2007, Bartz 2006).

We know that environment friendly lubricants are better known for its biodegradation, low toxicity, renewability and expulsion of specific substances(Bartz 2006),otherwise the environmental acceptability of lubricants generally encompasses a range of potential environmental benefits such as resource conservation, pollution source and emission reduction, recycling bath and so on(Pirro and Wessol 2001).

The use of Ecobadge or ecolabel encompasses biodegradability as the most important criteria for the environment friendly lubricants. Biodegradability means the tendency of a lubricant to be ingested, degraded and metabolized by micro-organisms. Complete biodegradability indicates that the lubricant has returned to nature. Partial bio-degradability generally indicates that one or more components of the lubricants are not degradable. To classify the lubricant as potentially bio-degradable, the degradation of ≥60% in 28 day must be reached according to the OECD 301metho ≥80% in 21 days according to CEC L-33-A-93 method respectively(Salimon at al 2010,Battersby 2000,Bartz 2006).

The toxicity and renewability are of great importance too. The toxic or R phase containing compounds are unallowed or their content can't be exceed by .1%(wt.).The fully formulated lubricant shall have the particular carbon content derived from renewable raw materials. This content in various ecolabels and lubricants categories can vary from 45 %(for grease) to more than 95% [chainsaw oils, concrete release agents and other Total loss lubricants (Rudnick-2009)].

The most important properties among the various lubricating oils are ecofriendliness and nontoxicity.

These properties we generally can found in the vegetable oils. Moreover vegetable oils have excellent tribological properties such as high flash points, lower friction coefficient, lower evaporation and high viscosity index in comparison with mineral based lubricants (Schneider 2006, Erhan and Asadanskos 2000,Miles 1996).

Contrary to that vegetable oils have some serious disadvantages. They are thermally less stable than mineral oils, more sensitive to hydrolysis and oxidative attack and their low temp. behavior is frequently insufficient(Salimon at al 2010,Schneider 2006).Low oxidation stability & pure low temp.behavior are the main problems for limiting usage of vegetable oils.

Among number of physico-chemical methods, to increase the oxidation stability, use of catalyst, emulsion method alkarylation, epoxidation, alkylation, acylation, hydroformylation, acyloxylation usually come in practice. All these methods are for increasing the thermoxidative stability. But unfortunately the substitution by these methods decrease biodegradability of vegetable oils making the choice between good technical properties and environmental benefits (Schneider,2006). Another method is to improve the performance by use of additives while restricting quantity, biodegradability, toxicity by Eco-labels.

Comparatively mineral oils based lubricants has good oxidative stability and excellent thermoxidative value causing better flash and fire points. The toxic emissions and degradation makes the environment polluted and hazardous for human beings and wilds as well, once they are released. The emitted gases convert themselves in to oxides and in to free radicals which also causes several respiratory tract diseases and disorders.

Thermal oxidation is minor practical based problem for vegetable oils, though there were a few studies related to properties of oxidized vegetable oils, can overcome subsequently (Fox & Stachowiak2003, Castro at al 2006, Mano at al 2009) however citation in this matter does not produce any anomaly taking Tribology & Environment both together. The use of denatured oil, impact on environment, poses serious threats afterwards, has not found anywhere (completely degradable).

The Purpose Of This Finding Is To Evaluate The Influence Of Thermal Oxidation On Physico-Chemicaland Environmental Edaphic Properties Of Seed Oil.

2. MATERIALS & METHODS

Conventionally refined, bleached and deodorized seed oil is obtained. Its oxidation is carried out using Rancimat743 apparatus.to that of the adopted standards of ISO 6886:2006.20 ml oil sample is placed in to a glass reaction vessel (no metals or catalysts) and heated up to 100°C. A glass tube is inserted from top to Setting up of the apparatus and subsequently working procedure of Rancimet743 was in parallel bubble dry air at flow rate of 10L/hr.

The exiting air is passed in to the measuring vessel along with the formation of volatile oxidation products. Measuring vessel is containing the deionized water, whose electrical conductivity is monitored by measuring cell. With the oxidation of the reaction material or seed oil, rapid production of volatile degradation product begins, so called Induction Period(IP).Volatile products dissolve in water and results in a rapid increase of electrical conductivity monitored by the Rancimat Apparatus.

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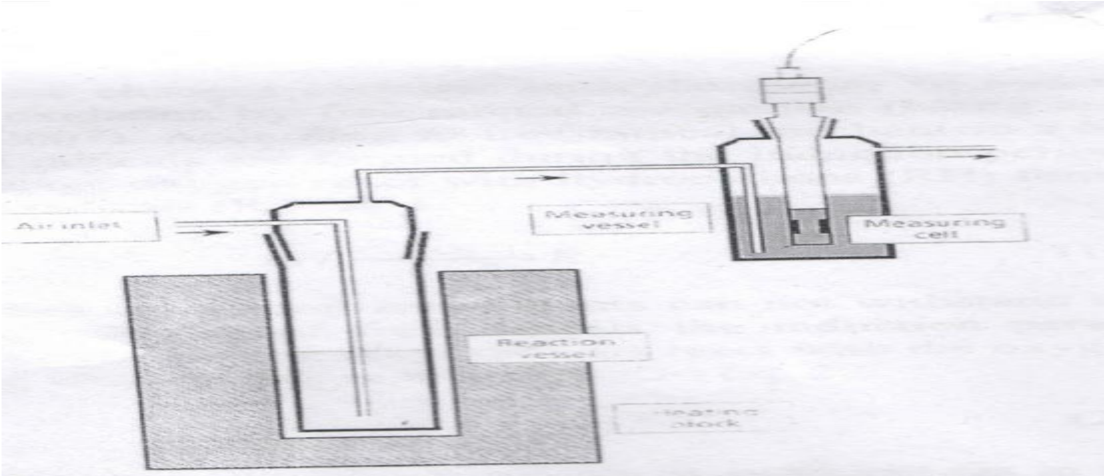

Fig 1. Principled view of Rancimat 743 oxidation performing cell

The four ball test rig was used to measure tribological properties of samples as in figure.

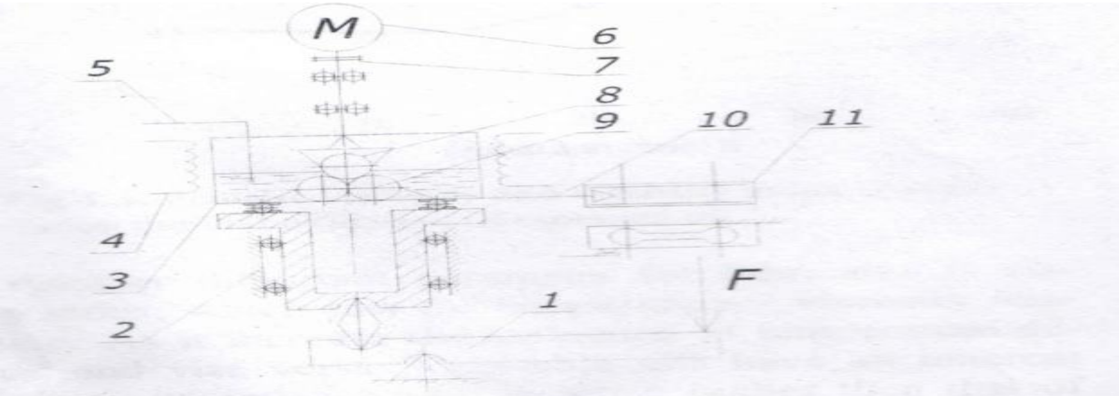

Fig 2. Schematics of Four-Ball tribotester: 1 – load transfer lever; 2 – vertical center bearing; 3 – oil sample compartment; 4 – oil heater; 5 – thermocouple; 6 – electric motor; 7 – clutch; 8 – upper rotary ball; 9 – lower stationary balls; 10 – torque transfer lever; 11- force transducer

The load of 150N was used. The test runs 1hour.

Prior to each experiment, all the appropriate parts of the machine,i.e.bottom and upper ball holders, oil vessel and the test balls were washed in an ultrasonic bath and then dried. The testing procedure was adapted from the standard DIN51 350 Part3.

The diameters of the wear scars on three stationary balls and the friction surfaces were measured and analyzed with an optical microscope. For each run the scar measurements were reported as an average of the Wear Scar Diameter(WSD) of the three balls in millimeters.

Kinematic viscosities of oxidized samples were determined 40°C & 100°C and viscosity index established according ISO 3104:1994 and ISO 2909:2002 respectively. The Ocean Optics USB4000 Visible light spectrometer set with xenon pulsed lamp PX-2 was used to determine absorption of the samples in all oxidation periods. The non oxidized seed oil was used as reference. The 200 ms integration period and 10 scanning samples average was chosen.

The biodegradability was measured according CEC L-33-A-93.Biodegradability of Two-Stroke cycle out board Engine Oils in Water. The biodegradation rate was measured using FT-IR spectrum RX I method, by disappearance of C-H bonds in 2930cm^{-1} wavelength.

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3. RESULT & DISCUSSION

During the oxidation of seed oil, its color changes from specific yellow to bright yellow at the beginning of induction period. Just after induction Period the oil became transparent and got a quite yellow at the end of 40 hours oxidation. The changes in seed oil transparency can be easily demonstrated using visible light spectroscopy (fig.-3).Taking the pure seed oil as the reference, the 20 hrs oxidized oil has dramatic changes in its absorbance.

There is one peak in 380 nm and one slope in 420nm wavelength. The wide range of these peaks show, that a lot of different compound are formed.

The disappearance of 420 nm slope in the 40 hrs. oxidized seed oil suggests that it is responsible for yellow pigment. At the same time the 380 nm peak becomes wider and moves a little bit to the longer wave side.

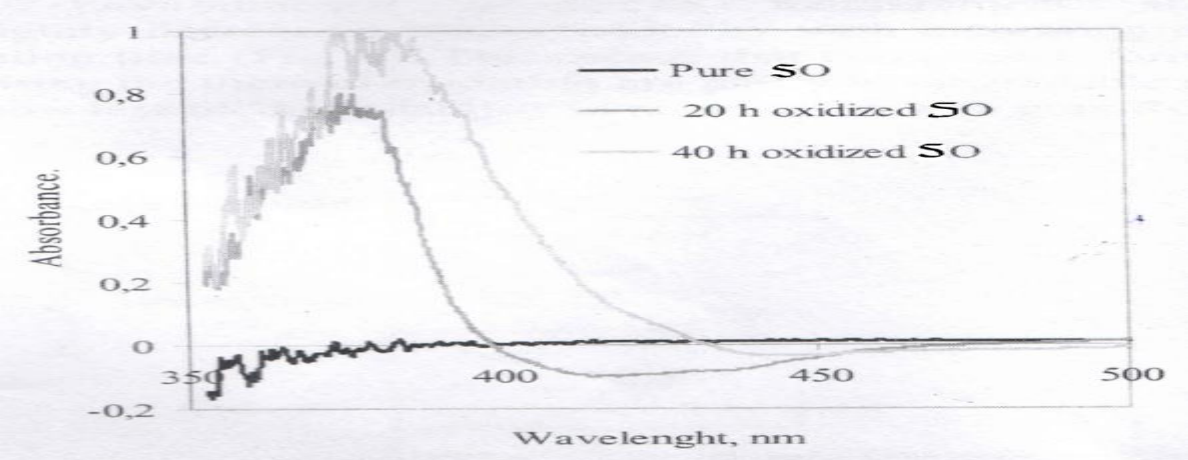
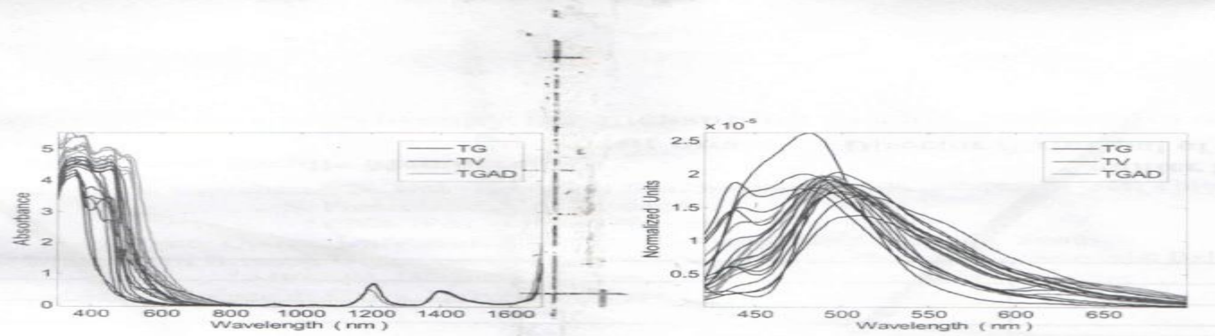


Fig 3. Optical spectroscopy of the pure and different tim
oxidized Seed oil

While for the case of lubricating oil obtained from the crude oil contains the undermentioned quality parameters & specification spectra.



igure 2. Spectral characterization of the lubricant oil collection: absorption spectra in the UV-VIS-NIR range (lef and intensity fluorescence measurements (right).

Data type	Spectral band (nm)	# PC	Explained variance
Fluorescence spectrum	420 – 700	4	99%
Fluorescence temporal decay	-- --	2	100%
UV-VIS absorption spectrum	290 – 800	4	97%
NIR absorption spectrum	1100 – 1690	3	99.5%

Table I. Spectral characteristics used for multivariate data analysis, and PCA specifications.

Quality parameter	R^2	SECV
Water content	0.843	56.8
JOAP-index	0.973	10.1
TAN	0.739	0.1
Phosphorus	0.969	527

Table II. PLS regression characteristics of the lubricant oil's quality indicators.

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All these measurements were performed by means of optical fiber based instruments that made use of L.E.D.'s or compact lamps for illumination and miniaturized spectrometers for detection,multivariate data analysis and to sucessfully co-orelate the wide optical spectral signature of lubricating oil to determine the important oil parameters such as TAN,JOAP-INDEX,WATER CONTENT & PHOSPHORUS and DEGREE OF DEGRADATION.

These changes coorelate with the theory of hydrocarbon oxidation by free radical mechanism(Mang & Dresel,2007).According to free radical mechanism a lot of alkyl radicals are formed,during the induction period.In this stage oxygen react with hydrocarbon(RH) forming free radicals($R^{\bullet}$),eq.(1).

$$R\text{-}H \xrightarrow{+O_2} R^{\bullet} \quad \text{------(1)}$$

When the natural antioxidants cann't withstand increasing quantity of free radicals the induction period finishes.

At this time alkyl radicals react with the O_2 forming alkyl peroxy radicals($RCOO^{\bullet}$) eq.(2)

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \quad \text{----(2)}$$

When the quantity of O_2 is sufficient (as in the case of Rancimat Test),the present reaction has an extremely high rate and a lot of alkyl peroxy radicals are formed.It seems fairly obvious that the end of induction period 420nm slope show the alkyl radicals.Following the oxidation mechanism it disappears in further oxidation.

After the induction period the polymerization and epoxidation takes place and the high molecular weight compound are formed.After the induction period,extremely increasing kinematic viscosity confirm the polymerisation process (fig.4).The increasing viscosity is undesirable in lubrication mechanisms because it can cause higher energy consumption & even failure at lower temp.

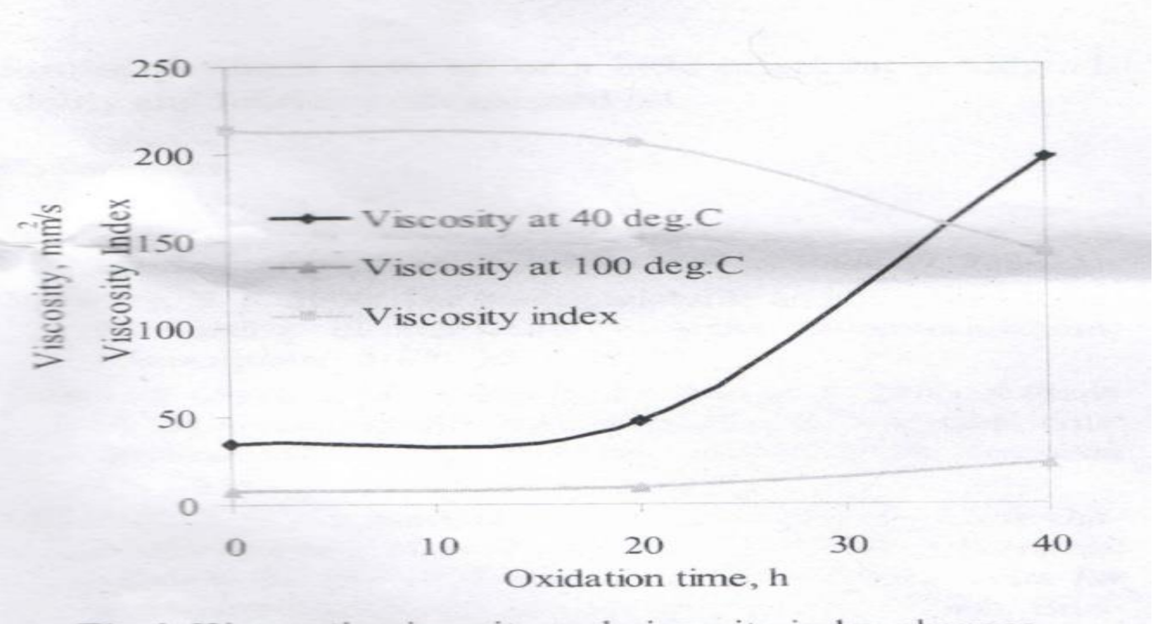

Fig 4. Kinematic viscosity and viscosity index changes during thermal oxidation of Seed Oil

Another important parameter for lubricants is viscosity index,which show the temp.-viscosity relationship. As the temp. decreases it increases and vice-versa.Vegetable oils have an inherent high viscosity index which is much higher than that of mineral lubricants.However thermal oxidation decreases the viscosity index of seed oil.The decrease can be related either to the formation of high molecular weight compounds or degradation of triglycerides.The tribological test result show only a little effect of oxidation time on wear reduction properties of seed oil, The 20 hrs oxidised seed oil having the highest level of free radicals show higher wear,so lesser lubricity.With this result we can predict that aging of seed oil till the end of induction period can cause maximum 20% increase.

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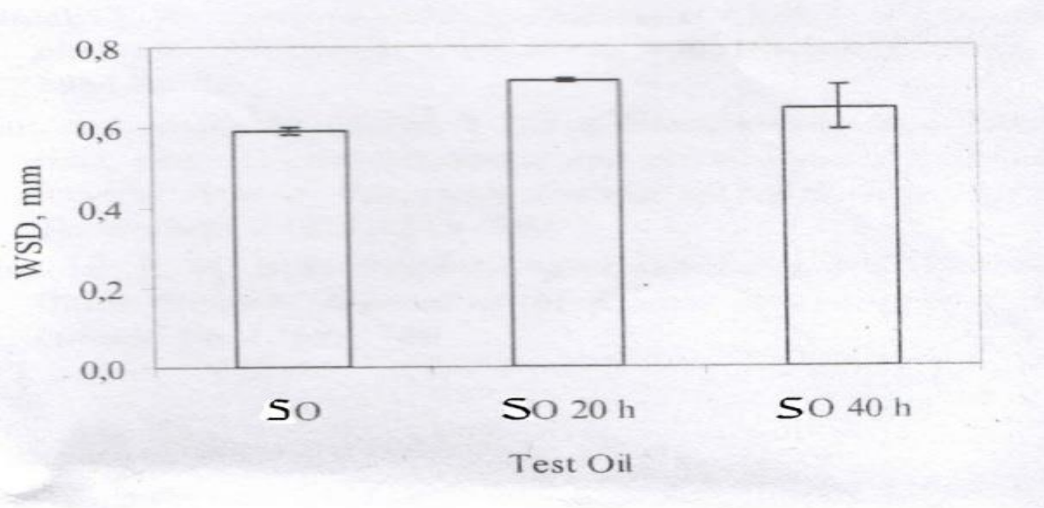

Fig 5. Lubrication properties of pure and oxidized SO.

The lubrication properties of 40 hrs oxidised seed oil can be affected by much more factors.At the first place there is an increasing viscosity which can lead to better lubrication layer formation.

The second one are high molecular weight product formed in the last stage of oxidation.They can lead formation of trobopolymers which also reduce the wear.

The lubricity can also be affected by degradation of triglyceride structure,decreasing viscosity index,increasing acidity and a lot of different nonradical products formation.The wear of balls lubricated with 40 hrs oxidised seed oil is worse than non oxidised seed oil.Nevertheless even long time oxidised seed oil do not cause dramatic increase in wear as can be expected from changes in chemical compositions.

Environmental properties measurement show slightly decreasing biodegradability with increasing oxidation time.This means that compounds formed during oxidation are partly biodegradable and show less biodegradability in comparison to pure seed oil.According to spectral anaysis,the 40 hrs oxidised seed oil has a lot of high molecular weight compound while 20 hrs oxidised seed oil has less.It is likely that high molecular weight compounds are less biodegradable.Despite that all investigated samples according to CEC-L-33-A-93 standard are readily biodegradable,whereas mineral based lubricating oil are not biodegradable and ecofriendly yet they are thermoxidative.

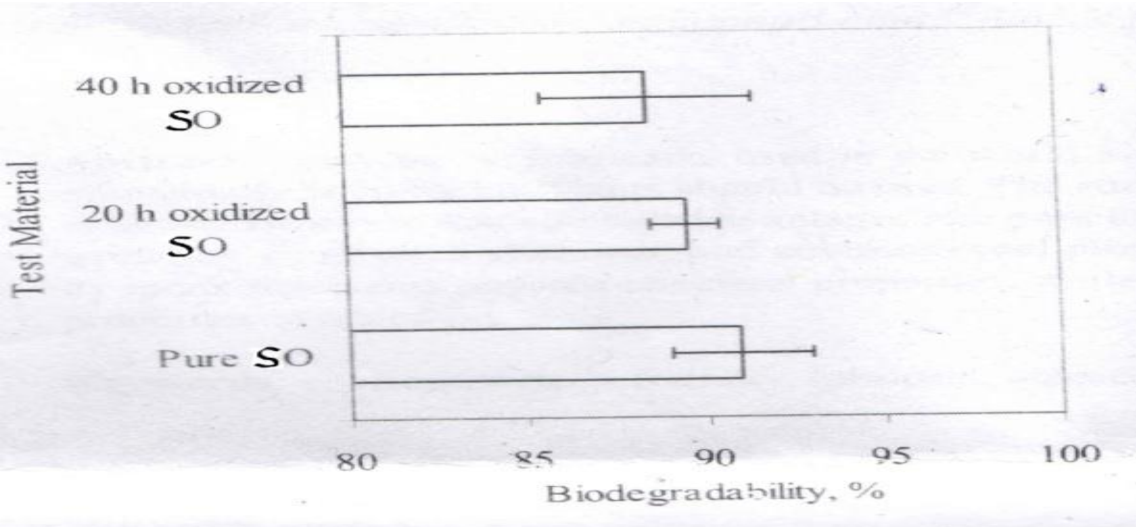

Fig 6. Biodegradability of pure and oxidized SO

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4. CONCLUSIONS

This comparative study concludes:-→

1. We can change the mineral based lubricating oil with the vegetable based lubricating oil.
2. Vegetable based oil are much more ecofriendly.
3. Though they are less thermoxidative yet biodegradable up to a maximum extent.
4. They can be considered as an nation economy booster.

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