

**INFLUENCE OF CRUDE METHANOLIC EXTRACTS OF RICE
HUSK AND SAW DUST AS ANTIOXIDANTS ON THERMO-
OXIDATIVE STABILITY OF BASE LUBRICATING OIL**



Ph.D. THESIS

Submitted by

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**INSTITUTE OF CHEMICAL SCIENCES
UNIVERSITY OF PESHAWAR, PESHAWAR, PAKISTAN
(MAY, 2015)**

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*A dissertation submitted to the University of Peshawar in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy in Chemistry*

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The thesis/dissertation prepared and submitted by Mr. Jan Ullah titled

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APPROVED BY

Supervisor

External Examiner

Director

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**IN THE NAME OF ALMIGHTY ALLAH,
THE MOST BENEFICENT,
THE MOST MERCIFUL**

DEDICATED TO MY BELOVED AND RESPECTABLE PARENTS

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LIST OF ABBREVIATIONS AND NOTATIONS

ASTM	(American Society of Testing Materials)
IP	(Institute of Petroleum)
RHE	(Rice Husk Extract)
SDE	(Saw Dust Extract)
MBO	(Mineral Base Oil)
DPPH	(Diphenyl Dipicryl Hydrzyl Radical)
LTO	(Low Temperature Oxidation)
HTO	(High Temperature Oxidation)
API	(Ammerican Petroleum Institute)
ZDDPs	(Zinc Dialkyl (aryl) Dithio Phosphates)
BHT	(Butylated Hydroxy Toluene)
DODPA	(Di-Octyl Di- Phenyl Amine)
MBDTBP	(Methylene-Bis-2, 6-Di-Tert-Butyl Phenol)
SAE	(Society of Automotive Engineers)
ISOVG	(International Standard Organization Viscosity Grade system)
IH	(Inhibitor)
PD	(Peroxide Decomposer)
NO _x	(Nitrogen Oxides like NO, NO ₂ , N ₂ O, N ₂ O ₃ , N ₂ O ₄ , N ₂ O ₅ etc.)
SO _x	(Sulfur Oxides like SO ₂ and SO ₃)
CO _x	(Carbon Oxides e.g. CO and CO ₂)
KV	(Kinematic Viscosity)
VI	(Viscosity Index)
VR	(Viscosity Ratio)
SF	(Stability Factor)
TAN	(Total Acidity Number)
CCR	(Conradson Carbon Residue)
IN	(Iodine Number)
C.st	(Centi-stoke)



NOT	(Number of Times)
TGA	(Thermo-Gravimetric Analysis)
TGDTA	(Thermo-gravimetric Differential Thermal Analysis)
DTG	(Differential Thermo-Gravimetry)
DSC	(Differential Scanning Calorimetry)
PDSC	(Pressurized Differential Scanning Calorimetry)
FTIR	(Fourier Transform Infrared Analysis)
UV/Vis	(Ultra-Violet and Visible Analysis)
OSI	(Oxidative Stability Index)
LSV	(Linear Sweep Voltammetry)
RPVOT	(Rotating Pressure Vessel Oxidation Test)
SEM	(Scanning Electron Microscopy)
EDS	(Energy Dispersive X-Ray Spectrometry)
NMR	(Nuclear Magnetic Resonance Spectroscopy)
GPC	(Gel Permeation Chromatography)
RH	(Rice Husk)
SD	(Saw Dust)
ν	(Viscosity Characteristics)
ρ	(Density)
PAI	(Peak Area Increase)
PH	(Peak Height)
OSI Time	(Oxidative Stability Index Time)
AOCS	(American Oil Chemists Society)
AOM	(Active Oxygen Method)
SF	(Stabilization Factor)
IP	(Induction Period)
T Onset	(Degradation Onset Temperature)
T Offset	(Degradation Offset Temperature)
GC –MS	(Gas Chromatography Mass Spectrometry)
t_R	(Retention Time)
CND	(Carbon Number Distribution)



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The undersigned further declare that the thesis is based on my own work, and has not been copied from other sources except where specifically referenced/acknowledged. The thesis meets the University policy of plagiarism.

Jan Ullah

Scholar



Influence of Crude Methanolic Extracts of Rice Husk and Saw Dust as Antioxidants on Thermo-Oxidative Stability of Base Lubricating Oil

ABSTRACT

Lubricating oil performs a variety of functions in an engine/machine. It provides lubrication to the moving, sliding & rolling surfaces thereby minimizing friction, wear, hence imparts more life to the machinery. In addition, it protects metal surfaces against corrosion, acts as heat transfer agent, flush out contaminants, absorb shocks and seal leaks. However, during service, it is exposed to high load, speed, heating & oxidation hence suffered from degradation and gets spent. The spent oil no longer retains its properties and needs frequent replacement with a new one which is not only a waste of valuable resource but also contributes to the environmental pollution if carelessly disposed off. Performance improvement additives (antioxidants) are added in commercial formulations to avoid or delay the oxidation and to increase the service life of the oil. However, the antioxidants developed to date have several shortcomings and suffer from antagonistic effects which decline their abilities to withstand oxidation. Therefore, there is a need to investigate about new antioxidants to be efficient enough not only to minimize the thermo-oxidative degradation of the oil, and increase its service life but also to avoid disposal issues. The present work aimed to evaluate the antioxidant potentials of two natural antioxidants i.e. alcoholic extracts from rice husk (RHE) and saw dust (SDE) in oxidative stability of base lubricating oil under a set of experimental conditions.

The oxidation stability of the mineral base oil with and without antioxidants was evaluated in an air atmosphere using temperature and time ramped oxidation experiments. The influence of a number of experimental conditions such as temperature, oxidation time, and concentration of each antioxidant was studied. The efficiency of the derived extracts at low and high temperatures was investigated. Mineral base oil (MBO), MBO additized with the RHE, and SDE were evaluated at different temperatures and times using modified IP 48 procedure. The effect of additive concentration was also



studied. With combination of the physico-chemical, conductimetric, spectroscopic, thermo-analytical, calorimetric and chromatographic analysis, the oil degradation in the absence and presence of the antioxidants under study was monitored.

Principal physico-chemical properties such as kinematic viscosity determined at 40 & 100 °C, viscosity index & viscosity ratio and complementary properties such as Conradson carbon residue, total acidity number & iodine number were determined using standard ASTM Methods. Oxidation may lead to formation of mostly carboxylic acids leading to changes in the spectroscopic properties of the oil. In order to know about the chemical changes occurring in the base oil during oxidation, FTIR analyses of the original oil, and un-additized MBO, RHE- & SDE-additized samples oxidized at optimum temperatures and time were performed in order to identify the oxidation products like carboxylic acids/carboxylates, amides, esters, etc. The conductance changes occurring in the oil samples during oxidation were recorded in order to decide about the oxidation induction times (OIT) and oxidative stability index (OSI). The changes were measured in case of the un-additized and RHE- & SDE-additized base oil samples oxidized at 100 and 200 °C for time duration of 06 h. Next to OSI analysis, the thermo gravimetric analyses (TGA) were performed in case of the un-additized and various additized base oil samples oxidized at 100 and 200 °C for time duration of 06 h in order to evaluate their thermal stabilities in terms of T_{onset} , T_{offset} , mass loss and weight gain. Calorimetric analyses in terms of oxidation induction time (OIT) were performed in case of the oil samples spiked with bio mass derived extracts in comparison to un-additized MBO in order to evaluate the antioxidant character of the RHE and SDE. To decide about changes in spectroscopic properties of the original and variously oxidized residual oil samples, Gas chromatographic- Mass spectrometric analysis was carried out in order to ascertain the changes in the individual compounds, the hydrocarbon range products and the hydrocarbon group type's distributions.

The results indicated that the antioxidants under study imparted stability to the base oil at low as well as high temperatures. The results further inferred that the use of biomass derived additives reduced the oxidative degradation of the base oil to a greater



extent and thus could be used on commercial scale to eliminate the use of environmentally objectionable and costly additives.

ORGANIZATION OF THE THESIS

The thesis is compiled in the form of **THREE** chapters.

1. INTRODUCTION

This chapter represents the theoretical knowledge about the lubricating oil, its composition, properties, base oil and its types, oxidative degradation, mechanism of oxidative degradation, method used to evaluate oil degradation, literature survey related to base oil degradation, and the role of antioxidants. All references cited have been given at the end of this chapter.

2. EXPERIMENTAL

This chapter is devoted to the various experimental and state of the art analytical methods used (ASTM/IP). All references cited have been given at the end of this chapter.

3. RESULTS AND DISCUSSION

This chapter presents the experimentally achieved results supported by the corresponding pictorials, graphical representations, spectra, thermograms, oxidographs and chromatograms discussed in the light of the available literature. The conclusions based on the results are also provided. All references cited throughout the text have been given at the end of this chapter.



CHAPTER # 1

INTRODUCTION



CHAPTER-1

INTRODUCTION

1.1. SCOPE OF THE THESIS

Commercial lubricating oil is prepared from base oil provided with performance improvement additives. The base oil is obtained from a variety of sources i.e. natural, and synthetic. The natural base oil is either obtained from plants & animals or from petroleum. Base oil obtained from crude petroleum by distillation is called mineral base oil. When the base oil is formulated with performance enhancing additives, then it is called packaged or formulated lubricating oil.

Formulated lubricating oil is widely used widely used to provide lubrication to the moving, sliding and rolling surfaces in order to minimize friction, wear and to impart more life to the machinery. In addition, it performs a variety of other functions in engines and machines. It protects metal surfaces against corrosion, acts as heat transfer agent, flushes out contaminants and absorbs shocks and seals leaks [1]. However, during service, it is exposed to high load, speed, heating and oxidation hence suffers from degradation and becomes spent after some time.

The spent oil no longer meets with the requirements due to inferior properties and needs to be replaced immediately with a new one. This replacement is not only the waste of money but also a loss of a valuable oil resource. Moreover, the spent oil is either incinerated or land filled which are environmentally unfriendly disposal methods.

Two pathways are involved for turning the lube oil used in an internal combustion engine into spent, either the lube oil undergo physico-chemical changes via oxidation, or it becomes contaminated with its own oxidized products, material of the combustion chamber and airborne originated dust. Among these, thermo oxidation is considered as the major cause of quality deterioration of lubricating oil. This is due to highly oxidized environment in the oil sump. In the presence of air at elevated temperature, the lubricating oil undergoes a series of free-radical chain reactions leading to formation of hydroperoxides [2-4]. Aldehydes, ketones, acids, and alcohols are also produced upon further reactions. These oxidation products polymerize into high molecular weight



materials resulting in the formation of sludges responsible for the undesirable change in lubricant properties, which then promotes the engine wear [5-8]. Degradation is also temperature dependent process which increases with the increase in temperature. Oxidation products are formed whose nature depends primarily on the temperature [9].

Oxidation in the engine can be minimized by using certain additives. Ample research is devoted throughout the world to the synthesis, technology and applications of different types of base lube oil additives [10-15]. However, such efforts are yet not fructified and concerted efforts are still needed in this regard. In spite of the extensive research on the issue, oil degradation is still considered as a major issue.

In order to curb the issue, research is devoted to the spent oil reclamation, which involves the conversion of waste oil into renewed oil [16-20]. However, the quality of the reclaimed oil is inferior and do not meet with the specifications. Moreover, such attempts have been found to be tedious, costly and environmentally objectionable.

The antioxidants developed till date do not meet effectively in service and the users still rely on frequent replacement of oil with a new one. Moreover, most of the lubricants and many of the additives in daily use are petroleum derived which are harmful to the environment, making it difficult for safe and easy disposal. There has been an increasing demand for green lubricants. Therefore, there is a need to investigate new antioxidants to be effective enough to minimize thermo-oxidative degradation of oil and to increase the service life.

In present work, antioxidants were extracted from natural and un-exhaustible sources like rice husk (or hull) and saw dust of *Pinus longifolia* which are waste products and produced in substantial quantities per years. The antioxidant was selected based on their composition with respect to the presence of phenolic compounds, aromatic amines, organic sulfides and furans. Rice husk alcoholic extract has been reported to be consisted of more benzenediols than sawdust [20-21].The antioxidant potential of phenolic compounds have been reported in the literature [22-23]. The extracts from both biomasses were obtained using methanol as solvent and subjected to antioxidant activity tests by DPPH Assay method in order to determine their antioxidants capabilities. The extracts were then blended with the lube oil samples under study in various concentration (1%, 2 %



and 3%).The oil degradation was studied both at low temperatures (LTO 25 °C & 100 °C) and high temperatures (HTO 150 °C& 200 °C) for different oxidation times (00, 06, 12, 18, and 24 h). The overall effect of temperature, oxidation time and concentration of antioxidants is presented.

1.2. AIMS AND OBJECTIVES

The aims and objectives of the present study are to,

- Ensure better and environmental friendly use of rice husk and saw dust which are considered as waste products in the rice mill/saw machine and often either burned in open or dumped on wasteland.
- Investigate the potential of certain biomass materials as source of new antioxidants for base lubricating oil stability.
- Study the influence of antioxidants under study and their concentrations on the oxidative stability of the base oil in terms of changes in physico-chemical, thermo-analytical, calorimetric and spectrometric properties at low and high temperatures.
- Increase the service life of base lubricating oil and hence to avoid frequent oil change by the users to save foreign exchange incurred on oil imports.
- Avoid/minimize the environmental problems associated with spent oil disposal.

1.3. LUBRICATING OIL

Any material which is interposed between moving parts of a machinery in order to promote smooth motion, and avoid friction & wear is termed as lubricating oil or a lubricant. Lubricant may be of natural origin, derived from crude petroleum or specially lubricants synthesized commercially for specific applications.

The vegetable oils and animal fats have been used for lubrication purposes in past many years owing to their excellent lubricity, far superior than that of mineral oil and



biodegradability. However, lack of sufficient oxidative stability has limited their use. These oils include olive oil, coconut oil, mustard oil, soyabean oil, etc.

Mineral oils are produced from naturally occurring petroleum or crude oil or their synthetic equivalents by distillation. Their properties depend largely on the quality and consistency of the crude oil from which it is refined and also on the refining process. Mineral lubricating oil is a homogenous mixture of hydrocarbons containing traces of sulphur, oxygen and nitrogen containing hydrocarbons. The raw lubricating oil also contains of waxes, hence the distillation fraction is further purified by extraction & by separating the waxes and then by hydro-finishing. The hydrofining involves contact with hydrogen at a high pressure and temperature, in the presence of a catalyst to remove sulfur and nitrogen. Performance improvement additives are incorporated before being provided to the market. Depending upon the application of lubricating oil, it has many categories including automotive lube oil, aviation oil, railroad lubricants, marine lubricants and industrial oil; turbine oil, hydraulic oils, cylinders oil, compressors oil, refrigerators oils, etc.

Synthetic oils are commercially manufactured for critical applications to perform correctly in extreme or difficult environments i.e. such as nuclear gas or other applications like vacuum and oxygen installations, hydraulic equipment and heat transfer in the high temperature range. Synthetic oils are characterized with no impurities, possessing high viscosity, better thermo-oxidative stability which led to their better and longer lasting performance. Semi synthetic oils which are blends of mineral and synthetic oil containing benefits of both mineral and synthetic oil are also used in certain applications [24].

1.4. FORMULATION OF LUBRICATING OIL

Commercial lubricating oil is prepared from base oil provided with performance improvement additives. A lubricant is the mixture of base oil and unfunctional and polyfunctional additives. The major component of engine oil is formulated with 70-79 % base oil and remnant is additives. Thus lubricant is homogenized chemically with hydrocarbons base oil as a backbone and chemical additives. Thus, lubricant major component is base oil; however, to improve service performance, it is formulated with performance improving additives. The resultant product is called packaged oil. The



additives regulate many important lubricant survival functions. The well-known additives in blended form with lubricant are antioxidants, antifoaming & cleaning agents, pour point depressants, dispersants, detergents, viscosity and viscosity index improvers, etc. [25].

For formulation of particular lube oil, some test specifications are conducted. These include; color, density, oxidative stability, flash point, fire point, pour point, aniline point, load carrying ability, API gravity, viscosity, viscosity index, total acidity number, carbon residue, iodine number copper strip corrosion, dielectric constant, etc. by standard ASTM and IP methods [26].

1.4.1. Production and Composition of Base Oil

Base oils are derived from three main primary sources. These are:

1. Crude oil
2. Chemical synthesis
3. Natural resources other than crude oil (fats, waxes, vegetables, etc.)

Owing to high cost of synthetic lubricants, today, lubricating oil derived from petroleum is the most commonly used lubricant in wide range of applications. In the proceeding section, how petroleum is converted into mineral oils that can be used as the base oil in lubricant products is discussed.

Crude oil is composed mainly of many different kinds of chemical materials almost based on carbon. The base oil is obtained from crude petroleum by fractional distillation followed by solvent extraction, de-waxing and hydro treatment. The composition may vary and based on the type of crude oil used & the refining conditions. The degree to which these processes are done defines the ultimate grade or quality of the final base oil.

Solvent extraction is carried out with sole objective to remove aromatics. Dewaxing involves the removal of paraffins having long chain, and high-melting points. Catalytic dewaxing is some time used to convert waxy material into iso-paraffins for improved properties. Hydrotreatment involves treatment of the base oil with hydrogen with the objectives to remove unsaturation or to remove aromatics.



The process schematic is given in Fig.1.

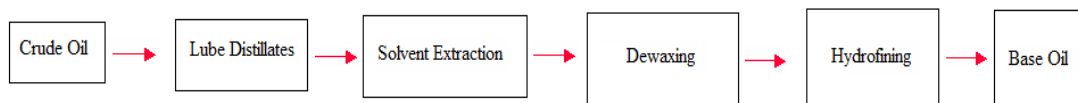


Fig.1.1. Schematic of the refining process used for base oil

The crude base oil mostly has carbon compounds having carbon number distribution in the range of 25 to 45. These are further classified into paraffins, naphthenes (or cycloparaffins), aromatics and heteroatom compounds. Straight chain paraffins and alkyl aromatics are unwanted in lube oil because of their poor cold flow properties and unstablity towards oxidation. Iso and chain cycloparaffins are desired due to high thermo-oxidative stability which lead to composition comprising of iso and cyclic paraffins (70—90 %) and aromatic (10-30%) [27].

In addition to hydrocarbons, some heteroatoms containing compounds are also present which need to be removed due to several detrimental effects. For instance, these may cause the oil to be unstable at elevated temperature. Moreover, these may interfere with viscosity index (VI). VI refers to the stability of viscosity vs. temperature; high VI oils are less sensitive, thinning less at higher temperatures. The following section explains the composition of the base oil:

n-Paraffins: Base oil contains n-paraffins having carbon contents of C_{18} and above. The paraffins in turn are comprised of many members of homologous series in the range having boiling point limit of 600 °F. These are obtained and concentrated to purity from waxy fraction of crude oil by solvent de-waxing. The n-paraffins can be easily identified and quantified by gas chromatography because these give sharp peaks in GC profile.

Iso-paraffins: These fall in same category of n-paraffins with alkylated branches particularly methyl and other higher ones. Identification of individual members of iso-paraffins is quite difficult by the use of GC-MS. The iso-paraffins are familiar to acquire high VI, low pour point and confer good oxidation resistance; therefore, it is one of the desired constituents of the base oil.



Aromatics: Benzene in particular and other polyaromatic hydrocarbons with two or more aromatic rings are well known minor ingredients of base oil. Alkylated aromatic rings especially on 1, 4 position are said to have high VI and good oxidation inhibition potentials. Fused aromatic rings (PAHs) are unwanted because these are environmentally unfriendly.

Sulfur Containing Compounds: Sulfur compounds may be thiols, sulfides, thiophenes, benzothiophenes, dibenzothiophenes and more complex configurations. Sulfur compounds are undesired in lube oil because their presence leads to catalyst poisoning during processing. Therefore, its concentration is reduced by solvent extraction and hydrocracking in refined lubes. The 2,6-dialkylated dibenzothiophenes are the most effective catalyst poisons for hydroisomerization catalysts and to nickel and other heavy metals based catalysts. These are very resistant to hydrotreatment. Other thiols and sulfides can easily be hydrogenated.

Nitrogen Containing Compounds: Nitrogen mostly exists as amine, amide, pyrrole, pyrrolidine, pyridine, and piperidine alkyl and aromatic analogs. Nitrogen compounds mostly contribute in color formation, therefore, can easily be reduced in degraded lubes. Hydrocracking process can minimize the nitrogen contents to several ppm. Special separation techniques are required for their removal.

Oxygen Containing Compounds: Oxygen compounds appeared as furans, alcohols, aldehydes/ ketones and carboxylic acids which rarely exist in fresh lubricants. However, these are abundantly present in degraded or spent oil obtained from automotive engines and other industrial machinery [28].

1.4.2. Classification of Base Oil

Base oil is classified on the basis of several properties (Table-1) in to three main groups discussed as under:

Group-I Base Oil: Group-I base oil contains maximum concentration of hydrocarbons (90 %) some aromatics (10 %) and least amount of sulphur compounds. It is the least processed oil which is obtained by solvent extraction refining techniques. These techniques



separate oil molecules based on size and removes waxes, aromatics and heavy metals present as harmful constituents.

The aromatics and sulphur compounds are considered undesirable which cause the insoluble high molecular weight degradation by products formation. This indicates higher risk of degradation and thus shortens the lubricant life cycle. Group-1 base oil is especially used in heavy duty applications for some automobiles [29].

Group-II Base Oil: Group-II base oil is also obtained by same process as followed for group-1 oils but instead of solvent extraction, they are hydrocracked. In hydrocracking, hydrogen is catalytically reacted with the base stock at extremely high temperature and pressure. This results in some events of molecular rearrangements including formation of paraffin isomers, cleavage of long chain naphthenic molecules and reshaping of aromatic rings formation. Thus, the N, S and aromatics contents are nearly eliminated from the base stock at the end of process [24].

Group-III Base Oil: These oils possess better properties than group-2 base oil because these are more severely treated at higher pressure, elevated temperature and longer processing time [24]. Group-II and III oils are more viscous with longer degree of stability in terms of more resistance to oxidation; experience less temperature induces viscosity change and least amount of sludge formation as compared to group-1 base oil. The major drawback associated with group-II and III base oils is their reduced capability to dissolve or suspend the polar essential additives and polar by products that formed as a result of degradation. Hydro processing and hydrocracking result in the reduction of aromatics and naphthenics contents that in turn decline the solubility of the base stock. Lubricant with high solvency is able to soap up polar additives and lock them in place. Base stock possesses the low solvency; it is unable or less able to soap up the additives polar compounds and polar oxidation by products [30]. Some properties of the base oils are listed in Table.1.1.



Table: 1.1.API Base Oil Classification

API -G	I	II	III
Viscosity, mm ² /s @ 100°C	3.7-3.9	3.8-4.0	3.7-3.9
Viscosity, mm ² /s @ 40°C	17-18	16.50-18.6	16.2-18.80
Viscosity Index	100-125	101-135	142-180
Volatility, wt. % (Noack)	24-27	22-25	14-16
Pour Point, °C	-5-(-15)	-10-(-18)	-12-(-21)
Aromatics, wt. %	15-17	0.6-1.0	0.3-0.8
Saturates, wt. %			
Paraffins wt. %	32.8-45	23.5-55	70-86.1
Cycloparaffins wt. %	35-50.2	42-75.9	10-13.6
Sulfur, wt. %	0.1-0.3	0-.01	0.005

Among the three base oils, Group III base oil, the most highly hydro-processed are currently of wide use thereby gaining importance as substitutes for current synthetics due to some desired properties in formulation including high oxidation resistance, withstand viscosity change at wide temperature range and less volatility The saturated compounds usually show more oxidation stability than the mono and poly aromatics and naphthenes [31].

1.4.3. Additives

The chemical substance added to bring about a new property or improve already existed property in base oil of a lubricant is termed as additive. A lubricant of best quality possess the properties like resistant to oxidation, thermal decomposition, corrosion, rusting & wear and better dispersive, cleaning, metal deactivation, pour point dispersion & viscosity modifying characteristics These characteristics are acquired with the use of certain performance and lubricants service life enhancing additives. Additives raise useful life and assign additional performance characteristics to the lubricant, such as improvement



in flow, modification in friction, and resistance to oxidation, thermal degradation and prolong the pressure stability.

In the formulation of a best lubricant, the base oil is mixed with certain additives in a specific concentration as a blend to meet with the environmental, economical and commercial challenges [33]. Some additives work antagonistically and some synergistically but it must be effective in terms of performance at any operating condition. Without these additives, modern engines would cease to perform satisfactorily, for example the sulphuric acid produced in diesel engines reacts with the lubricating oil in an oxidative manner to form oil insoluble products that adhere to metal surfaces. When the engine is cooled below the dew point of water, the acid may also attack metal surfaces. The acidic products present in oils may be controlled by the addition of basic additives such as antioxidants, dispersants or metal deactivators. Generally, the additives package in engine oil 5-30 % in terms of weight which perform abundant functions for oil in various parts of engine. The conventional additives used in the commercial lubricants are summarized in Table 1.2 [34, 35]. Among these antioxidants are of great concern.

1.4.3.1. Antioxidants

Antioxidants serve to slow down or inhibit lube oil oxidation or degradation which otherwise result in deposits/sludge and polymer formation, viscosity increase, corrosion, etc. This group of additive can be further subdivided into two classes, peroxide decomposers and radical traps or propagation suppressors.

1.4.3.1.1. Peroxide Decomposers

This class consists of phosphites, sulphides and most frequently encountered, zinc dialkyl (aryl) dithiophosphates (ZDDPs). ZDDP is a multifunctional additive, being a metal passivator, an extreme pressure additive and a peroxide decomposing antioxidant. ZDDPs possess synergistic nature and mainly used for their antioxidant and anti-wear abilities [36]. It is discovered that ZDDP's retard bearing corrosion by two mechanisms, peroxide decomposition and the formation of a protective film. Secondary alkyl ZDDP's were found to be more effective corrosion inhibitors than primary alkyl ZDDP's because



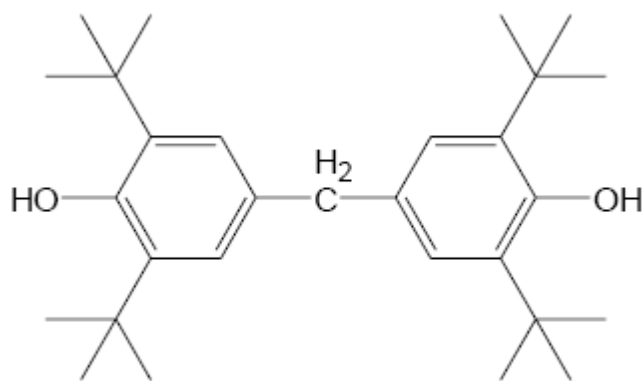
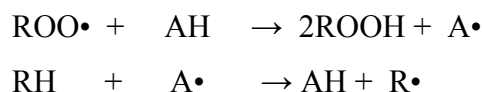
they can be more easily decomposed. The protective film formed on the bearing surface is known to be a decomposition product, because on examination, proportionally more zinc was found than phosphorus and sulphur. The surface film helps to reduce oil oxidation by preventing the formation of organo-metallic compounds that act as catalysts for the oil degradation processes.

It is well established that the addition of ZDDP to a model hydrocarbon oxidation system did not alter the overall extent of oxidation and inhibition process existed in distinct stages. The first being the decomposition of the hydro-peroxide, which results in the complete consumption of the ZDDP, forming a disulfide and un- identified products. The second stage is the inhibition period, where peroxy radicals are trapped by decomposition products. This was followed by a second hydro-peroxide decomposition stage, where the concentrations of the disulfide and 'unknown' are depleted to form radicals that initiated further oil oxidation, at an accelerated rate [37].

1.4.3.1. 2. Radical Traps or Propagation Suppressor

The important classes of antioxidants used to inhibit the propagation step include phenolics (simple phenols and hindered phenols) and aromatic amines (secondary alkyl arylamines and diarylamines) which serve as radical scavengers. The inhibition mechanism undergo competition for peroxy radicals with the substrate (RH), hence, shortening the kinetic chain length of the propagating specie in a rate-determining step by hydrogen-atom transfer to the peroxy radical. Hindered phenols may be mononuclear, such as 2, 6-di-*tert*-butyl-4-methylphenol (BHT) or may be polynuclear like bisphenols, diphenols, and polyphenols. Steric hindrance is imparted to phenols with at least one bulky alkyl group, which reduces the ability of a phenoxyl radical to abstract a hydrogen atom from the substrate and produce an alkyl radical that is capable to initiate oxidation. The inhibition activity of antioxidant molecules can be improved by introducing long aliphatic chains which decreases their volatility and increases the stability. Aromatic antioxidants for instance *p*-phenylenediamine and diphenylamines are highly effective than phenolics due to their larger scavenging ability for peroxy radicals [4, 38]. Some compounds behaved as synergist for arylamine Dioctyldiphenylamine (DODPA) like sodium acetylacetonate.

When it is combined with aryl antioxidant, it effectively reduces the viscosity rise and TAN increase in the lubricant [39]. Organomolybdenum complex such as molybdenum dialkyldithiocarbamates act as peroxide decomposer and acquire synergism with diphenyl amine i.e. work as anti-wear and antioxidant [48]. Phenolic antioxidants combine with hydro-peroxide and form the stable cyclohexadieneone. Phenolic and aryl amine antioxidants suppress the propagations reactions of oil degradation by capturing the peroxy radicals and form the stable compounds. Hindered phenolics; 3, 5-di-*t*-butyl-4-hydroxytoluene (BHT) and 4, 4-methylene-bis-(2, 6-di-*tert*-butylphenol) [MBDTBP] depicted as under:



The aryl amine molecule scavenges four peroxy radicals per amine molecule while phenol molecule traps two peroxy radical phenolic units. It indicates the more effective antioxidant potentials of aryl amine than phenolic ones [40]. Engine oil having phenolic or aminic antioxidant and organometallic complexes shows better performance [41].

**Table: 1.2. Conventional Additives Used in Lubricating Oil**

Additive type	Purpose	Functions	Example
De-emulsifiers	Separate water from oil	Hydrophilic part attracts water and prevents it from emulsion formation with oil.	alkoxylated phenol alkoxylated amines alkoxylated glycerol and alkylsulfonates
Antifoams	Inhibit lubricant from synthesizing long live foam.	Keep surface tension of the oil and allow the separation of air bubbles which prevent foam formation.	Polymethoxysiloxane
Antioxidants	Slowdown or inhibit oxidative breakdown	Prevent free radicals and terminate radical reactions.	Mono/poly phenols, alkyl aryl amines, organo- P/S/Mo compounds
Antiwar and extreme pressure agents	To avoid or decline friction and wear	Prevent metal-metal contact by reacting chemically with metal to form film with lower shear than metal.	
Corrosion and rust inhibitors	Prevent interaction of humidity with lube oil	Adsorb on to metal surfaces to form a hydrophobic film, preventing water and air reaching the metal surface.	High molecular weight carboxylic, sulphonic or phosphoric acids and their salts,
Detergents	Keep oil appearance clean	Neutralized the sludge and varnish precursors by reacting chemically thus keep them soluble.	sulfonates, phenates and salicylates.
Dispersants	Keep dispersed the insoluble contaminants 0-200 nm in liquid lube oil medium as oil soluble micelles	Contaminants are prevented from clustering and kept in the suspension by the dispersant molecules by polar attraction which connect the contaminants to the dispersants	Amines succinimides and succinate esters.



Metal deactivators	Reduce metals catalytic effect on rate of oxidation	Promote inactive film formation on metal surfaces by combining with metallic ions (e.g. iron and copper).	
Pour point depressants	Ensured the lubricant to flow at low temperature	Interlocking effectively and results in young growing crystals precipitation from solution at lower temperatures.	copolymer of ethylene and vinyl acetate and polymethacrylates
Viscosity modifiers	Decrease temperature dependency of viscosity.	Increasing thickening power of oil with temperature rise, minimizing its effect on the viscosity.	acrylate polymer, olefin polymers and styrene butadiene copolymers

1.5. CLASSIFICATION OF LUBRICATING OIL

The Society of Automotive Engineers (SAE) has classified the lubricating oil as under:

1.5.1. Single Grade Engine Oil

The engine oil possessing single maximum value of temperature at which it is used for safe and effective engine protection. SAE made eleven single grade viscosity classifications including SAE 0W, SAE 5W, SAE 10W, SAE 15W, SAE 20W, SAE 25W, SAE 20, SAE 30, SAE 40, SAE 50 and SAE 60. The symbol W implies the winter which confirm its use at winter season at a specified given temperature limit. Other engine oils without W indicate are used in both winter and summer seasons. The lower the number, lower will be the operating temperature at which it works effectively in engine. Higher the number reveals the useful protection of engine and operating machines at high temperature and high load condition. Single grade lubricating oil acquires limited range of operating temperature condition that's why these have un-extensive uses.



1.5.2. Multi Grade Engine Oil

Multi grade engine oils have two seasons operating temperatures limits. These have two numbers used for winter and summer season, respectively. The first number before W shows the temperature of winter at which it works effectively. The second number after W indicates the maximum temperature limit to be used at summer for its well protected performance in engine. These are SAE 5W-20, SAE 5W-30, SAE 10W-30, SAE 15W-40 and SAE 20W-50. Lower is the first numerical number reveals more better would be its performance from that low temperature to the upper limit. The major benefit of multi grade oil is their extensive use both at winter as well as in summer. Multi grade oils have some other categories including multi grade gasoline engine lube oil, multi grade diesel engine lube oil, multi-grade aviation lube oil and multi grade marine lube oil [42].

The base lubricating oil used in the present research work is employed to formulate multi grade SAE 20W-50 of diesel engine heavy duty category due to its abundant use especially for the transport of heavy load [43].

1.6. DEGRADATION OF LUBRICATING OIL

Oils are required to lubricate the systems used in a variety of machinery not only to enhance the performance but also to impart more life to the machinery. However, during service oil in sump is always exposed to heat, shear and environmental contaminants. These agents accelerate the oil degradation. The mechanism of oil degradation is discussed in the proceeding section.

1.6.1. The Mechanism of Oil Degradation

In this section, a brief outline of the fundamentally more important liquid phase hydrocarbon oxidation reactions are given, as applied to a general hydrocarbons. The general reaction scheme in the liquid phase is primarily considered to be a free radical process [44]. The separate steps that, as a whole make up hydrocarbon oxidation reactions are initiation, propagation, branching and termination. The oxidation processes in the liquid phase can be catalyzed by metals or inhibited by several different mechanisms. Each of these steps is discussed individually as under:



1.6.1.1. Initiation

The first step in the overall mechanism is the initiation of free radical species. Several possible reactions exist, and under certain conditions each one can predominate. Firstly, simple cleavage of the hydrocarbon molecules to form two radicals can begin the process, when the parent molecules are exposed to light or heat. Thermal energy can cleave a hydrocarbon molecule depicted as under:



Where: RH is an alkane

A more probable source of free radicals is realized when the sump oil in an engine is saturated with oxygen. Oxygen abstracts a hydrogen atom from the hydrocarbon [43] depicted as under:



This results in to a hydro-peroxy radical. It has been stated that reaction 2 proceeds very slowly below 150 °C, but at higher temperatures, this is likely to be the predominant cause of initiation [45]. The general consensus regarding the magnitude of the average activation energy for the initiation reactions is reported to be 146-272 kJ/mol [45, 46]. This excludes reaction 1 from playing a major part in the overall process, because the energy required on average to cleave a C-H bond is 426 kJ/mol and that required to cleave a C-C bond is approximately 356 kJ/mol. It has been mentioned previously that an internal combustion engine provides a hostile environment for lubricating oil, owing to the presence of blow-by gases in the sump region. The gases that have been blown past the piston rings possess a high concentration of un-burnt fuel and unstable mixtures of nitrogen oxides, which are vigorous oxidants and may contribute to initiation [47].

1.6.1. 2. Propagation and Degenerate Branching

Propagation reactions involve the consumption and regeneration of a 'chain carrier' that is formed in an initiation process. Degenerate branching reactions comprised of the



decomposition of an intermediate molecular species (formed from the parent hydrocarbon) as an additional source of free radicals which give rise to a secondary initiation of reaction chains. The reactions of free radicals generally have low activation energies relative to molecular decomposition or oxidation. The first propagation reactions are those that produce peroxy radicals and the corresponding peroxides depicted as under:



Other propagation reactions appropriate to relatively high temperatures (750 K) and therefore, characterized in gas phase oxidation studies includes:



The approximate energy of activation for the reactions (3) is 4 to 8 kJ/mol, for reaction (4) 40 to 60 kJ/mol, for reaction (5) is 40 to 60 kJ /mol and for reaction (6) is 30 kJ/mol. The most important propagation reactions in an engine environment are probably reactions (3) and (5), which produce the hydroperoxide free radicals. At temperatures below 250 °C, organic peroxides form the basis of many degenerate chain branching reactions. At the temperatures encountered in the upper ring zone, they may decompose to form aldehydes and alkoxy radicals, which can initiate further chains, leading to a more complicated mixture of stable intermediates and final products.

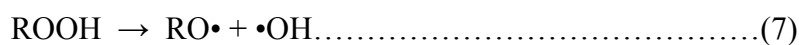
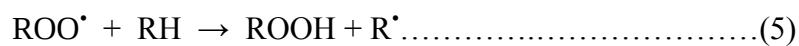


-

In some cases, the peroxide reacts to form low molecular weight carboxylic acids. Thus, the oxidation products i.e.the carbonyl compounds are the major precursors for the high molecular weight sludges. It is also reported elsewhere that sludge formation by adding potassium hydroxide to oil can be eliminated. It is originated that the acids



oligomerised in the presence of oxygen to form dimers and trimers (no higher molecular weight material was formed in the absence of oxygen), which then polymerized to form the oil insoluble sludges. One of the studies reported that as the molecular weight increased, the number of conjugated bonds increased, these always being conjugated to the carbonyl group. The polymeric products were found to have regular repeating groups, and as the size of the molecule increased so did the number of ketonic groups, these being formed by free radical attack on the C=C bonds [48]. The higher molecular weight alkenes decomposed more rapidly than paraffins with an equal number of carbon atoms. This is because the pi bond is a prime target for free radical attack, the activation energy for an addition to the pi bond being 1-30 kJ/mol. Some workers have proposed a reaction scheme for the oxidation of paraffins, initiated through the formation of peroxy radicals followed by the production of alkoxy radicals, depicted as under:



Reaction (9) was only assumed to occur in conditions containing very small amount of oxygen, which prevents the oxidation of alkyl radicals to form alkylperoxy radicals. This can, therefore, be excluded from the reaction scheme assumed to occur in an engine environment, owing to the excess of oxygen available. Reaction (8) was considered to be part of a larger reaction scheme that demonstrates one route to the vast numbers of products formed in a hydrocarbon oxidation reaction. The molecular product of reaction (5) was assumed to react in the following fashion:



The peroxy radicals produced in reactions (11) and reaction (12) combine as given in reaction (8). Reaction (7) is considered to be degenerated chain branching reactions because it acts as a secondary source of initiating reactions. It is also reported that the



reactions of the alkoxy radicals leading to formation of alcohols, esters, ketones, aldehydes and ethers [49]. A primary alkoxy radical could undergo the following reactions:



Or



A secondary alkoxy radical could give rise to:



And



Finally, for tertiary alkoxy radicals, the reactions could be:



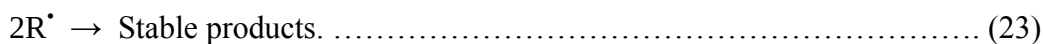
Or



These reactions further demonstrate the ease with which a myriad of compounds can be produced in an oxidative environment [50]. Many of these reactions will proceed very easily, because the dimerization of radicals (and combination reactions in general) does not require energy of activation.

1.6.1.3. Termination

These reactions involve the destruction of the free radical chain, by the recombination of two the free radicals to form a non-chain-carrying product, or by the reaction of a free radical with the surface of the reaction vessel (engine). There termination reaction is depicted as under:





The rate constants of radical recombination (termination) reactions were given by Walker [51] to be 10^8 to 10^9 mol/lit/sec at a temperature >100 °C. The termination reactions compete with the propagation and branching reactions for free radicals. If the termination reactions are ineffective the oil would degrade very quickly. The rate of oil degradation can be slowed further by the addition of antioxidants [52].

1.6.1.4. Inhibition

Many hydrocarbon base stocks exhibit a limited degree of inhibition but their antioxidant qualities are not as effective as those of the specific additives added to the formulation to retard the oxidation processes. Phenolic inhibitors are a natural class of antioxidant which functioned as breaking the peroxide chain given as under:



And



Further, inhibition reactions might involve the reduction of the hydroperoxide, by a sacrificial mechanism, such as:



Oxidation inhibition by peroxide decomposer can be explained as:



Therefore, after sometime, the oil got degraded [53].

1.6.2. Factors Affecting Oil Degradation

There are a number of factors responsible for oil degradation and its rate. These include oxygen environment, temperature, composition of the base stock and the presence of catalysts.

1.6.2.1. Oxygen Environment

Lubricating oil in sump is exposed to oxygen. The availability of oxygen environment for chemical reaction increases as the oil becomes more aerated by circulation



through the sump. The oxygen availability is also increased by the air present in the exhaust gases blown past the piston rings into the crankcase or engine. Rate of thermo-oxidative degradation with amount of oxygen is related by linear relationship [54].

1.6.2.2. Temperature

The oil temperature can vary considerably throughout the engine, from 60 to 80 °C in the sump and 110 to 140 °C at the bearing surfaces, to in excess of 200 °C in the literature. The heat is removed from the hot metal surfaces by the oil. As the temperature of the oil rises, its viscosity is reduced, producing a corresponding drop in the minimum oil thickness between the working surfaces. Over the temperature range 60 to 80 °C, per °C, temperature rise causes a reduction in film thickness of 1 %, which in turn means that the working surfaces reach a higher temperature and the oil is subjected to larger shear forces.

Compressive heating and thermal degradation usually occurs when base oil comes in contact with hot surfaces of the machinery parts. It is also observed when there is sudden rise in temperature concerned with adiabatic compression of entrained air bubbles in pumps, bearings and other under pressure sites. The oil film or layer alters chemically when come in contact with hot surfaces or with compressed air bubbles. The temperature of the lubricant is of prime importance in machinery working environment. The lubricant must also dissipate heat in addition to keep the moving parts of engine or machinery separated from each other, this means that the lubricant are sometimes heated to temperature higher than the recommended stable temperatures [55]. Such overheating generally leads to vaporization of the light ends in the lubricant as well as its decomposition. This in turn causes the removal of certain additives from the system without performing their job or may result in undesired increase in viscosity of the lubricant [56].

At elevated temperatures that exceed the thermal stability point of the lubricant, larger molecules are cleaved into smaller ones. This thermal breakdown of larger hydrocarbons is often termed as thermal cracking or thermal degradation, which can further induce several side reactions like favors polymerization, produce gaseous by-products, deplete additives and produce insoluble sludge. Most often the thermal



degradation is associated with decrease in lubricant viscosity due to the formation of lower olefins.

Sometime an air bubbles transition occur from the zone of lower pressure to the higher pressure which promotes the adiabatic compression, referred as pressure-induced thermal degradation or microdieseling. This may produce hot zones having temperature above 1,000 °C, which further leads to formation of carbonaceous by-products and speed up the oil degradation.

Linear relation is found between rate of degradation and temperature rise and its rate becomes double at each 10 °C increase in temperature. The dominant visual color change appeared for lubricant due to thermal or compressive heating and oxidative degradations. The change in color extensively observed because of formation of chemical carbon and oxidized products [47].

1.6.2.3. The Composition of the Base Stock

The composition of the base stock is governed mainly by the crude oil source, the method and the degree of refinement. The oxidation stability of the base stock is probably its single most important performance criterion from the point of view of chemical reactivity. The oxidation reactions are influenced by the nature of the saturated and aromatic fractions, including the naturally occurring sulphur compounds. The in-service performance of the oil is affected by the additive package added, which usually constitutes 5 to 30% of the total lubricant. However, each component added to improve one property may adversely affect the other one. The saturated compounds usually show more oxidation stability than the mono and poly aromatics and naphthenes [57].

1.6.2.4. The Presence of Catalysts

Many materials can act as an oxidation catalyst, the most common being particulate metals, organometallic compounds or free radicals in blow-by gases. Metals can have a catalytic effect on the oil oxidation processes, whether they exist in solid particulate form or in solution. It has been stated, however, that the efficiency of a metal catalyst is directly dependent on the rate of oxidation and dissolution of the metal surface into the oil. It may



be inferred that the catalytic effect of metals depends not only on the base stock, but on the antioxidant package. For example, zinc to possess a high catalytic activity) when present in zinc dialkyl (aryl) dithiophosphate (ZDDP) is a very effective antioxidant and metal deactivator. When oil got linked with copper or iron contact surfaces, the initiation reaction takes place at lower temperature. Metal cations can catalyze the chain branching step [47, 54].

1.7. ADVERSE EFFECTS OF LUBRICATING OIL DEGRADATION

The ultimate consequences of lubricant degradation are the viscosity increase, corrosion and insoluble resinous sludge along with varnish formation. The corrosion and viscosity increase alter the operating conditions and other side products causing deleterious effects which lead to machinery failure. Sludge and varnish formation promote deposits that can interfere with the oil flow resulting in wear and corrosion. Lubricant degradations experimentally observed to be due to three causes; extensive thermal shock, compressive heating and oxidation [56].

1.7.1. Acidity and Viscosity Enhancement during Degradation

At low temperature, the oxidation of hydrocarbons gives alcohols, peroxides, water, aldehydes and ketones. Carboxylic acids are formed as a result of aldehyde or ketone oxidation which reveals that lubricant becomes more acidic [47]. The decomposition of longer hydrocarbon chain to smaller molecules decreases the viscosity of lubricant. But actually, lubricant viscosity increased during oxidation because of the condensation and polymerization of aldehydes and ketones at its significant level. These Aldol condensation reactions lead to formation of oligomers and low molecular weight polymer that promote increase in lubricant viscosity. The reduction in lubricant molecular weight caused by chain separation that form aldehydes, ketones and carboxylic acids and thereby counteracted by increase in viscosity due to Aldol condensation. Thus, in early stage of oxidation, slight drop of viscosity occurs but as the oxidation process progresses, the effects of condensation dominate which results in overall increase in lubricant viscosity [56-60].



1.7.2 Sludge and Varnish Formation

The solubility of by-products of oxidation is very low in un-oxidized part of the lubricant. They possess major concentration of aromatics contents which are quite different chemically from the rest of lubricant which contain naphthenic and paraffinic oil molecules. The oligomer become insoluble in un-oxidized portion of the lubricant and separated from the oil in formation of sludge and deposits formed as a result of chemical changes. Aldehydes and ketones acid or base catalyzed Aldol condensation form sludge precursors which give high molecular weight products on further chemical reactions. An increase in viscosity due to these products which on mutual combination furnishes sludge and varnish production. Sludge formation is usually specified as insoluble in the bulk oily portion deposits formed characterized by thin lining on metal surface called varnish or lacquer [57, 61-64]

1.7.3. Nitration, Sulphation and Soot Formation

Soot is a by-product formed from the incomplete combustion of fuel in automobile engine and other industrial fuel based machinery. Soot formation cause viscosity increase and clogging of filters and oil galleries. Soot formation mainly attributed to oxidation of aromatic content of base oil possessing high molecular weight which causes the frequent oil flow in engine parts [57]. Exposure of hydrocarbons molecules to the environment of elevated temperatures and pressure in presence of N_2 and O_2 not only results in oxidation by products but also some nitrogen oxides (NO_x) like NO , NO_2 , N_2O_3 , N_2O_4 , etc. These NO_x are acidic in nature, therefore, causing build-up of varnish lacquer formation. Oxidation of sulphur contents of petroleum based lubricants or its inclusion in lubricant as chemical additives give rise to the formation of SO_2 and SO_3 which may catalyze sludge and varnish formation. These may lead to catalyze further degradation. SO_x when chemically united with H_2O vapours form H_2SO_4 that cause acid rain which has abundant deleterious effects on climatic changes, plants, animals, aquatic life, forests, materials, soil, infrastructure, etc. [65-69].



1.7.4. Hydrolysis of Ester Type Base Oil

Ester possesses high affinity for water to react that give carboxylic acids and alcohols as products which in turn enhance the acidity of ester type base oil. This increases the corrosive power of oil and catalyze oil breakdown further.

1.8. CHARACTERIZATION/ METHODS USED FOR EVALUATING OXIDATIVE DEGRADATION

The degradation phenomenon is assessed or evaluated by conducting the various physico-chemical, thermo-analytical and spectrophotometric techniques. These are presented in details as under:

1.8.1. Physico-chemical Tests

1.8.1.1. Kinematic Viscosity (ASTM D 445)

Kinematic viscosity is measured by using Ostwald viscometer, which is a U shaped calibrated tube, having a capillary tube in between the two bulbs. The viscometer is submerged in paraffin oil bath maintained at constant temperature. The bath oil is heated to the desired temperature of 40 °C or 100 °C, the sample is introduced into the tube and allowed to flow freely under gravity through the tube. The flow time between the two marks through the calibrated section of the viscometer is noted. The viscosity in unit of centistokes (cSt) is determined by multiplying the flow time (seconds) of sample with the calibration constant of the viscometer.

Viscosity measured at 40 °C has the industrial importance and when determined at 100 °C is employed for engine oil applications. ISVOG (International Standard Organization Viscosity Grade) system classified the viscosity of industrial oil that is the average viscosity at 40 °C. While for engine oils viscosity is classified according to Society of Automotive Engineers (SAE). Lubricants need to have a definite viscosity to give adequate operation on the equipment surfaces where they are employed. Viscosity change occurs when the oil gets oxidized which is an important parameter for the purpose when the oil condition is to be monitored i.e. whether fit or to be replaced. Viscosity is one of the most important parameters of the oil. Viscosity determination provides a particular number to compare the original recommended oil with the oil in service, an



undesired viscosity change (+ or – 10 %) usually act as sensor of lubricant degradation. Increase in viscosity is generally associated with:

- Increase in quantity of suspended solid material like wear particles, contamination, or soot
- Adulteration with higher viscosity oil
- Degradation of lubricant

A decrease in viscosity may reveal:

- Contamination from fuels, water, or fluid of process
- Adulteration with lower viscosity oil
- Shear of additives

1.8.1.2. Viscosity Index (ASTM D2270)

The Viscosity Index (VI) is an empirical number that indicates the effect of change of temperature on the viscosity of oil under study. A low VI signifies relatively large change in viscosity with the temperature. Viscosity generally decreases with the increase in temperature. Viscosity Index is referred to the maintenance of viscosity over a range of temperature. A relatively small change or no change in viscosity with temperature is indicated by high viscosity index, whereas low viscosity index shows relatively large change in viscosity with temperature. Fluids affected by temperature extremes have a low viscosity index, while fluids that maintain viscosity have a high viscosity index. The quality of lubricant is the function of viscosity index values i.e. oil classified possess the quality of low, medium, high and very high if its viscosity index values are 35, 35-80, 80-110, 110-n respectively. VI Improvers as additives and base oil of high quality are extensively used currently which raises the VI attainable beyond the value of 100. VI ranges 80-400 for the synthetic oil of aromatic type or mixed type o having paraffins, naphthenes and aromatics. Electronic calculators are presently used for the calculation of VI of an oil from its viscosity determined at 100°F (37.8 °C) and at 210 °F (98.9 °C) [69].

1.8.1.3. Stability Factor/ Viscosity Ratio (ASTM D445/ IP 71)

Stability Factor (SF)/ Viscosity Ratio (VR) is the ratio of kinematic viscosity (ν) of oxidized lube oil and that of original (un-oxidized) oil. KV of both oil samples is



determined and then its ratio provides the degree of degradation. VR value greater than a unit indicate that degradation has been taken place

1.8.1.4. Total Acid Number [(TAN) (ASTM D974, D644)]

Total acidity number (TAN) is expressed as milligrams of KOH consumed per gram of the sample (mg KOH/g). TAN value depends upon the amount of acids generated as a result of thermo-oxidative degradation. Larger is the TAN value, higher will be the level of degradation. TAN is also helpful to measure the acidic constituents present in lubricating oil. As additive, rust inhibitors are added to oil which in turn are acidic and can contribute to increase the acid number of the packaged oil. In addition, extreme pressure (EP) additives can cause high initial TAN-values. Test results of the oil after degradation are usually reported in comparison with the fresh oil in order to determine the changes occurred. High TAN values are indicative of the fact that the lubricant has been suffered from degradation, its useful life is over and it needs replacement with a new one. TAN values above 4.0 mg KOH/g are considered to be detrimental. Rapid changes in TAN in most cases can also be caused by oxidation from local heating, prolonged air entrainment or additive depletion as reported earlier [70, 71].

1.8.1.5. Iodine Number ASTM D- 1959

Iodine number (IN) is the amount of iodine in grams that react with 100 grams of the lube oil sample (cg/g) under specified condition. IN really determine the extent of unsaturation in sample which indicates extent of degradation due to cracking of sample at elevated temperature. The iodine number is used to measure the amount of unsaturation present in an oil or fat sample. Animal and vegetable oils and fats (triglycerides) contain long chains of carbon atoms bonded with hydrogen. The triglycerides may be saturated and unsaturated. In turn, the unsaturated triglycerides may be monounsaturated and polyunsaturated. Iodine can combine with fats that have unsaturation (double bonds) and, therefore, the number of such bonds can be deduced from the amount of iodine with which they will combine [72].



1.8.2. Thermal Analysis

1.8.2 .1. Thermo-gravimetric Analysis (TGA-D6370, D5967)

This analysis shows onset of degradation temperature and terminal degradation temperature of the lubricant or antioxidant under test that can be confirmed from TG curve. The TG curve is a plot between weight losses of hydrocarbons as a function of temperature. Higher weight loss indicates high volatility of the sample and low stability of test sample. The point in TG profile where the curve is started is the onset degradation temperature and the point in curve where it get ends and converted to a straight line is terminal degradation temperature. TGDTA analysis gives information about thermal stability of both lube oil and that of the antioxidant. In other words, vaporization temperature or decomposition point of sample under study can easily be identified as a strong endothermic peak in the TG profile. TG analysis is undertaken by using instrument called Thermogravimetric Differential Thermal Analyzer (TGDTA). TG profile is useful in understanding the mass loss or residue left of the analyte with temperature rise. Actually, in TG profile, the first large peak characterizes the initial degradation temperature and the other temperature at which this peak culminated is the final degradation temperature. While DTG curve reveals the onset decomposition temperature, initiation of exothermic peak, optimum temperature base of peak and the terminal degradation temperature which is end of exothermic peak. The weight loss in nitrogen environment is due to evaporation of the volatiles and decomposition of the matrix. While the weight loss in air environment attributed to evaporation, decomposition and oxidation of the oil. The difference observed in weight loss in N_2 and O_2 environments clarifies the amount of oxidized products in gaseous phase [73-80].

1.8.2.2. Differential Scanning Calorimetry (DSC)

DSC analysis is used to determine the oxidative stability of lube oil and the antioxidants. DSC curve is a plot between energy flow mW and the temperature in $^{\circ}C$ which contain the exothermic peaks. The study is conducted by using Differential Scanning Calorimeter where a sample is ignited in oxygen or nitrogen atmosphere. Oxidative induction time (OIT) is measured which is defined as the time at which the onset



of oxidation of a test specimen exposed to an oxidizing gas at an elevated test temperature is observed from steepness in the curve. OIT is used as an index to estimate about the relative stability of materials towards oxidation. It is also used as a quality control test in evaluating the effectiveness of various antioxidants added to a variety of materials, for instance polymers, lubricating oils, greases and edible fats & oils.

OIT measurements are usually conducted with temperature programming using differential scanning calorimetric technique, which involve the temperature programming of the sample in an open pan from ambient to a test temperature in the presence of an inert atmosphere. When the desired temperature is attained and equilibrium is established, the purge gas (i.e. air or oxygen) is used as oxidant and the stop watch is started, the time taken from the first oxygen exposure (t_o) to the onset of the oxidation (t_{onset}) is considered as the OIT value. Oxidation or thermo-oxidative degradation is achieved as an exothermic peak. The temperature program used to achieve the OIT test conditions is made up of two parts. The first part concerned with the constant rate of temperature rise from ambient to the test temperature, this gives the oxidation induction temperature (OIT) characterized by a large exothermic band. The second part deals with the establishment of the isothermal test temperature which is maintained to the termination of the experiment. In order to have meaningful results and to reduce the analysis time, the ramp rate to the isothermal test temperature is set as high as possible taking care to avoid overshooting the test temperature. The isothermal test temperature is carefully selected to produce OIT values in time range of 15-100 minutes. The higher value is selected in order to limit the analytical time & to increase productivity, and the lower value to limit the effect of measurement imprecision. The temperature can influence the OIT, the higher the test temperature, the lower is the OIT value. The typical isothermal test temperatures range is reported to be between 150 and 210 °C with minor temperature adjustments depending upon the material being tested. In case of a thermally stable material, OIT value may be quite long. Some time, it is desired to reduce the analytical time; the test temperature is then sometimes elevated. In case of PDSC, the OIT test is conducted under different experimental conditions compared to conventional DSC. In PDSC, the sample under test or trial is pressurized with the reactive oxygen gas at room temperature, followed by temperature programming to the desired test temperature at a constant rate. The initial time



for the OIT measurement (t_o) is recorded when the programmed temperature reaches the test temperature (T_o). The presence of exothermic peaks in DSC curve is indicative of oxidation of hydrocarbons and combustion [81-91].

1.8.3. Spectroscopic Analysis

1.8.3.1. Fourier Transform Infrared Analysis (FT-IR) (ASTM-E2412)

Infrared spectroscopy is a useful a spectroscopic technique used to study compositional changes occurring in a material upon oxidation. Further, it can be used to monitor additive depletion, formation of organic degradation by-products and various contaminants in the spent lubricating oil. It is also helpful in identifying the degradation mechanism responsible for the fluid degradation. Briefly, its significance in area of degradation involved various analysis given as under:

- FTIR analysis is carried out to decide about the presence of oxidized products as a result of degradation [92-102].
- This analysis also undertaken for finding degree of degradation which is confirmed from the area under the IR peak [103].
- Another useful application to understand the carbonaceous deposits due to oil degradation [47].

The FTIR analysis region ranges 4000-400 cm^{-1} which is divided in two categories. The functional group region 4000-1600 cm^{-1} and the finger print region ranges 1600-400 cm^{-1} . The oxidized products of degradation give peaks in the wave number range of 1900-1600 cm^{-1} due to carbonyl group ($\text{C}=\text{O}$) or in the range of 3600-3200 cm^{-1} because of OH group that represent alcohol or hydro-peroxide formed from paraffin oxidation. The stretching vibration peak may appear in the range of 1000-1200 cm^{-1} attributed to O-C examines the alkoxide group of paraffinic ether or aromatic ether due to alkyl aryl ether. The general FTIR spectra consist of various peaks observed at 1300-1450 cm^{-1} reveal CH_3 bending vibrations while for same CH_3 stretching vibrations the peak appeared at 2700 cm^{-1} . Other peaks for CH stretching obtained in the range of 3200 – 2850 cm^{-1} and peaks



between 1500- 1600 cm^{-1} show stretching vibrations. All these peaks represent paraffin constituents of the lube oil [104].

1.8.3.2. Ultra-Violet and Visible Analysis (UV/Vis)

UV/ Vis study is conducted for different purposes in analyzing the thermo-oxidative degradation of lube oil [38].

- Color change of lube oil which is an indicative of degradation due to oxidation, high temperature exposure and irradiation. Deepening in color is associated directly with the extent thermal degradation [105,106].
- Presence of aromatics as constituents of lube oil in its composition that decide the formulation of lube oil and level of degradation, the decrease in its amount examined the extent of degradations.
- Investigate the level of antioxidant activity of plant extracts that used as antioxidants in lube oil which confirm the hindered phenols and aromatic amines acting as primary antioxidants [108].
- In lubricating oil and in Nut shells determined the conjugated and aromatic contents which is 10-30 % in lube oil formulations. Larger is the aromatic content of lube oil better will be its quality because these are much resistant to degradation.

1.8.4. Miscellaneous Analysis

1.8.4.1. Oxidative Stability of Lubricant by Oil Stability Index (OSI) (RANCIMAT-743)

An American Oil Chemists Society (AOCS) approved method is the oxidative stability index used to find out the resistance to oxidation of oil or fat sample. This method has replaced the active oxygen method that requires more attendants, chlorinated solvents and remained inconsistent from place to place.

A method for assessing oxidative stability is the oil stability index (OSI) (16–19; also frequently termed the “oxidative stability index”. The OSI method is based on



determining the time (usually termed “ oxidation induction time”) before the maximum rate change of oxidation by measuring the increase in conductivity or decrease in pH of deionized water caused by dry air bubbled through a heated sample that carries the resulting volatile acids into a separate container with the deionized water. Oxidograph resulted which is a plot between the time and conductance or pH change consist of curve from which OSI time is noticed [104]. It is the indication of oxidative stability of the oil sample. OSI analysis is employed for the oxidative stability of oil in terms of its service life and the effectiveness of antioxidant under test [109, 110].

1.8.4.2. Linear Sweep Voltammetry (LSV): ASTM D6971

LSV test is used in order to detect the oxidative stability of a lubricant by measuring the primary antioxidants in the sample. This test is performed using an instrument called “RULER”. The level of remaining additive, and thus remaining useful life of the lubricant, is determined by comparison with levels of the control sample. The results of LSV can be correlated to oil degradation, provided a significant amount of data is available from that particular oil type.

1.8.4.3. Rotating Pressure Vessel Oxidation Test (RPVOT) (ASTM D2272)

One of the important properties of lubricating oil is its oxidation stability or resistance towards thermo-oxidation. The RPVOT test (previously RBOT) is carried out in order to determine oil stability towards oxidation. The test is used to measure the performance of the remaining antioxidant(s). The experimentally obtained results are compared with control sample. This method has limited value as a primary RCA test because fluid degradation may take place on isolated segments of the lubricant, causing insolubles to be created without meaningful drops in RPVOT values.

1.8.4.4. Scanning Electron Microscope/Energy Dispersive X-Ray Spectrometer (SEM/EDS)

SEM/EDS is used for textural, morphological and elemental analysis. The method employs a high-energy electron beam reflects off the surface of an object providing



detailed three-dimensional visual observations, while also identifying the object's elemental composition. This technique can be used in examining the deposit formation in any fluid including lubricating oil.

1.8.4.5. Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR is an analytical tool used to study the molecular properties of the lubricant. NMR may be ^1H NMR and ^{12}C NMRA. Lubricating oil is comprised of both hydrogen and carbon, hence both are used satisfactorily for its analysis.

1.8.4.6. Gel Permeation Chromatography (GPC)

GPC is also helpful in analysis of fresh and spent lubricating oils. The technique involves physical separation of the sample by the molecular size of its components. It is a promising tool for the study and separation of high molecular weight materials from the base oil, additives and formulated lubricants. These materials include many of the oxidation condensation high molecular weight products.

1.8.4.7. Spectro-chemical Analysis (ASTM D6595, D5185)

Spent oil may contain wear metals, airborne dust, internally generated contaminants, and certain additives. Elemental spectroscopy can be used satisfactorily to measure and monitor the specific trace metals generated due to wear. Particles detected are typically 8 μm or less and the results are reported in parts per million (ppm) by weight.



1.9. LITERATURE REVIEW

Degradation of lubricants is one of the challenging issue and has been majorly studied from the 20th century till date. Past research was focused on the following factors which influence the degradation behavior of base oil in order to find out ways and means to avoid its frequent degradation and to develop remedial measures.

1. Type of degradation; oxidative degradation and thermal, evaluation of thermo-oxidative stability of lubricant, composition of lubricant, mechanism of degradation, wear metals as catalyst for degradation.
2. Factors effecting rate of degradation; temperature, pressure and ageing or mileage.
3. Effect of fuel, moisture and other contaminants from engine or external source on degradation.
4. Type of base oil; mineral, synthetic and semi-synthetic or mixture of both.
5. Characterization and degree of degradation in laboratory as well as in various zones of engine or industrial machinery.
6. Use of antioxidants for avoiding degradation either synthetic or natural. Mechanism of prevention of degradation in the presence of antioxidants, synergism of antioxidants in lube oil, optimization of conditions for the better performance of antioxidants in lube oil, investigation of thermal stability of antioxidants in lube oil, kinetic, rheological and thermodynamic behavior of lube oil and its blends with antioxidants.

In the up-coming section, many researchers/scientists contributed in analyzing the above aforementioned factors and the updated advancements as a result of ample research are presented briefly. These summaries will enable the new readers to understand the degradation of lubricants in absence and presence of antioxidants.

Garrote *et al.* subjected rice husk and corn cobs to hydrothermal treatment in polar solvent medium (dichloromethane DCM) to obtain the products having potentials of abundant applications. The compounds were then identified with GCMS which were divided into four categories including sugar derived compounds, lignin derived



compounds, nitrogen containing compounds and fatty acids. The results showed that sugar derived products contained alcohols, aldehydes and ketones having concentration 595 and 1065 mg/kg of the sample for rice husk and corn cobs, respectively. Lignin derived compounds were phenolics with concentration 1111 and 1800 mg/kg for rice husk and corn cobs, respectively. The nitrogen containing compounds obtained were pyridine, pyrole and pyrrocarboxyldehyde whose concentration found were 23 and 34 mg/kg for rice husk and saw dust, respectively. While the fatty acids resulted were: myristic acid, stearic acid, palmitic acid, oleic acid and linoleic acid possessing the concentration of 111 and 143 mg/kg in case of rice husk and corn cobs, respectively. As a whole, total antioxidants concentration obtained from rice husk was 1222 and from corn cobs 1943 mg/kg in terms of natural phenolics and fatty acids [21].

Kramer *et al.* studied the influence of composition of group 1 and 2 base oil on the oxidative stability. The group 1 and 2 base oils were prepared possessing 1 % aromatics and less or almost undetectable amounts of sulfur and nitrogen using hydrofinishing catalyst combination. The coupling of inherent low aromatic contents and compounds having absence of hetero atoms imparted them the superior stability relative to group 1 base oil. It was found that aromatic concentration primarily influenced the oxidative stability. Oxidative stability was influenced by saturates especially the paraffin and polycyclic naphthenes when aromatic contents approached zero [30].

Adhvaryu *et al.* performed the liquid phase oxidation of five base oils and determined the sub-fractions of their hydrocarbons using modified IP 306 test procedure. The base oils were selected so as to cover a wide range of physicochemical characteristics. In order to assess the compositional and structural details, the base oil samples were qualitative as well as quantitatively analyzed using chromatographic (column, HPLC) and spectroscopic (MS, NMR, FTIR) ones. The structural changes and oxidized materials were also studied that were associated with thermal degradation. The results showed that poly-aromatic and naphtheno-aromatic compounds were suffered from more oxidative degradation than saturated molecules. The deposits and oxygenated polar compounds formed were originated from aromatic structures, which decreased as weight percent of the total base fluid as oxidation progresses. Alkyl substituted aromatic structures showed



larger decrease in chain length than purely paraffin (*n*- and *iso*-) compounds during oxidation. Spectroscopic data also indicated that alkylation of aromatics was mainly attributed to alkyl radicals generated as a result of thermal shock from long chain alkyl aromatics [57].

Duangkaewmanee *et al.* determined the synergistic and antagonistic effects with the four sulfur-, phosphorus and heavy metal-free antioxidants, hindered bis-phenol (HP), octylated diphenylamine (ODPA), octylated phenyl- α -naphthylamine (OPANA) and toluotriazole (TZ) derivative, on the oxidation stability, thermal and physico-chemical properties of dioctyl sebacate oil. The oxidation stability was investigated using a rotary bomb oxidation tester (RBOT). The results from isothermal and catalytic RBOT oxidation tests revealed that ODPA has an antagonistic effect on the OIT. The combination of HP:OPANA:TZ showed the highest and most synergistic antioxidant activity. Furthermore, through thermogravimetric analysis (TGA), synergism was evaluated in terms of both oxidation and thermal stabilities [61].

Reda reported the thermal stabilities of some antioxidants in pure oil and their blends in canola oil, in order to evaluate resistance to oxidation. The techniques used included thermal gravimetric (TG) and differential scanning calorimetry (DSC) at the temperature ranging from ambient to 250 °C. A number of antioxidants were studied in the present work including ascorbic acid, sorbic acid, citric acid, sodium erythorbate, BHT (3,5-di-*tert*-butyl-4-hydroxytoluene), BHA (2, 3-*tert*-butyl-4-methoxyphenol), TBHQ (tertiary butyl hydroquinone), PG (propyl gallate), phytic acid antioxidant and the SAIB (sucrose acetate isobutyrate) additive commonly used in oil. Among the antioxidants used, citric acid, sodium erythorbate, BHA, BHT, TBHQ and sorbic acid were suffered from decomposition at temperature below 180 °C, and therefore, have found to be associated with little protective action in case of the oil under test. On contrary antioxidant including phytic acid, ascorbic acid and PG, were found to be the most resistant and showed their decomposition at temperatures range of 180- 200 °C. They inferred that the SAIB antioxidant is the most resistant to oxidative stress and it can be used as a useful antioxidant in oils, improving their stability towards oxidative degradation [69].



Gamlin *et al.* described that the modern automotive engines formulated lube oil contained the hydrocarbons base oil as major constituent and several additives package as minor ingredient. However, the lubricant ultimate performance primarily dependent over the base oil quality, therefore, understanding the degradation behavior has taken key importance. In this research project, the thermo-oxidative decomposition of natural, fully synthetic and semi synthetic base oil was evaluated. The degradation of these base oil samples were characterized using conventional isothermal and modulated TGA and PDSC methods. From the results, it was concluded that base oils with higher viscosity within the same grade tend to degrade at higher temperatures. TGA isothermal analysis (at 170, 210 and 270 °C) showed larger T onset for natural base oil than fully and semi synthetic base samples. Non-isothermal PDSC with constant heating rate resulted the higher self-ignition temperature for the natural base oil than the fully and semi synthetic base oils. Isothermal PDSC observed for natural base oil gave higher OIT values with respect to the fully and semi synthetic base oil sample [74].

Jain *et al.* determined the oxidation stability of gear formulated oil spiked with antioxidants. The oxidative stability of the lube oil samples were assessed with DSC, TGA, RPVOT, micro-oxidation and IP48 methods. The effect of different antioxidants on the thermo-oxidative properties of gear oil was evaluated. As observed by all the techniques, the aminic antioxidant gave better thermo-oxidative stability than the phenolic antioxidant [76].

Jayadas *et al.* assessed the thermo-gravimetric analysis (TGA) of coconut oil, sesame oil, sunflower oil and the commercial 2T oil under nitrogen and oxygen environment to study their thermal and oxidative degradation. Reduction in weight gain after subjecting oil to TGA treatment was used as degradation sensor. The three common antioxidants not only shifted the TGA onset to higher values but also caused the significant decrease in weight gain in antioxidants doped coconut oil samples when compared with pure non doped coconut samples. Coconut oil showed lower weight gain, an indicator of oxidative stability, under oxidative environment than other sunflower and seasame oil antioxidants blended samples. The results showed the larger thermo-oxidative stability of



coconut oil than other oils under test. This can be attributed to the predominantly saturated nature of its fatty acid constituents [80].

Perez evaluated the oxidative properties of various lubricants using thermoanalytical methods such as PDSC and TGA. The lubricants samples analyzed were SAE multi-grade 10W30 automotive lubricating engine oil and the raffinate crankcase oil. The changes in antioxidants, its original unchanged amount and the remaining useful life of lubricant were determined with RULER method. The OIT time observed for the original lube oil was shifted to longer value than for raffinated used oil as clear from the PDSC analysis. The TGA curve showed the larger volatility loss for the used raffinate oil when compared with the original lube oil. RULER analysis suggested the higher concentration of antioxidants in original lube oil than in used raffinate sample. All these results of lower OIT value, higher volatility losses and lesser concentration of antioxidants revealed the degradation of raffinate oil than original lube oil [89].

Sitton *et al.* studied that antioxidants and elevated temperature efficiency criteria of lubricants used in modern turbines. The results obtained with RULER (per ASTM D-2272) showed that turbine lubricants with single antioxidant system possess better reproducibility and repeatability as compared with RPVOT method of oil testing with complex synergistic antioxidants. Fresh and spent oils of gas and steam turbine were used for the evaluation of effects of antioxidant chemistry on RPVOT based results [94].

Basu *et al.* have determined the appropriate oil change at different intervals. They developed an oil condition sensor which can be used to measure the electrical properties of engine oil. They correlated the electrical properties to the physical and chemical properties of the oil under test. They discussed the degradation of the oil under study, described sensor operational principles and correlated the sensor output with their physical and chemical properties [111].

Cerny *et al.* determined the oxidative stability of eight engine oils SAE 15 W-40 using the IP modified IP 48 method. Eight engine oils of specifications Agip, BP, Esso, Mogul, O^o MV, Petro-Canada, Shell, and Total were collected and oxidized. Chromatographic methods were used for their fractionations, group composition of base



oils and VI plus other additives amount were determined. In the collected samples, several differences in of oxidation stability were observed. Parameters such as viscosity characteristics, carbon residue, acid number, amount of pentane insolubles and mass losses were chosen for investigation of oxidation stability. Blended from a hydrocracked base oil was found to be the most stable [112].

Turner *et al.* used the electrical techniques like changes in dielectric and magnetic properties of the oil as methods of measuring the lube oil degradation. This work reported that distance travelled is not a useful indicator of the condition of the oil in terms of its viscosity change. Changes in magnetic properties of oil occurred as the oil get degraded. However, the dielectric properties were comparatively correlated well with viscosity and it is suggested that this could promote the basis of a good sensing technique [113].

Cerny *et al.* studied the oxidative stability of base oil and commercial heavy duty engine oil using thermo-analytical method PDSC. The lube oil samples analyzed were heavy duty engine oil with specification SAE 5W-30 and various other hydrocrackate and solvent neutral fractions base oil. PDSC techniques in both isothermal and non-isothermal were evaluated following the ASTM standards D 6186 and /or E 2009. Generally, from isothermal PDSC at 200 °C, the OIT obtained for about 50 different types of engine oils was in the range of 30-50 min. The OIT value showed decline with mileage for the engine oil attributed to the depletion of antioxidant. The non-isothermal PDSC was conducted for base oil because of its low OIT (5 min) at 200 °C isothermal condition, therefore, non-isothermal found to be a suitable method. The OOT (oxidation onset temperature) appeared for the synthetic base oil was much larger than natural base oil. Moreover, the BHT antioxidant synthetic base oil blend exhibited large OOT than natural base oil BHT blend [114].

Santos *et al.* characterized the automotive mineral lubricants after thermal degradation with spectroscopic techniques like FTIR, NMR, XRF), rheological (Rheometer, viscometer) and thermoanalytical (TGA and DSC) techniques. The spectroscopic, rheological and thermoanalytical properties of degraded and non-degraded mineral lube oil were compared. The lube oil (SAE 40W) was oxidized for oxidation time



1-48 h at temperature 150-210 °C. The results of FTIR and NMR showed the presence of degraded products in oil samples. TG curve showed decrease in TGA onset temperature for oxidized samples than fresh sample. DSC results indicated decline in the initial oxidation and combustion temperature along with increase in peak area in case of degraded oil when compared with the fresh lube oil. In general, increase in degradation temperature increased the viscosity of lubricant [115].

Karagozet *al.* investigated wood biomass (saw dust) and non- wood biomass (rice husk) oil obtained as a result of hydrothermal treatment with GC-MS analysis. Liquid products were obtained using different solvents such as ether, acetone and ethyl acetate. The compositions of oils (ether extract) from sawdust and rice husk comprise of both phenolic compounds and furans. However, phenolic compounds were the major ingredients of the extracted oil. Rice husk derived oil consisted of more benzenediols than sawdust derived oil. The rice husk oil contained 94% phenolics and 79 % in saw dust oil. The rest of the compounds identified were; aldehydes, ketones and carboxylic acids both found in rice husk and saw dust. The major phenolic compound found was methyl phenol in concentration of 25 % in rice and 19 % in saw dust. The other major constituent was benzenediol, the concentration of which in rice husk was larger than in saw dust [116].

Jian *et al.* studied the molybdenum complex (MC) an oil soluble additive which was synthesized and its complex with *p*-dioctyldiphenylamine (*DODPA*) was used in the formulation of synthetic lubricant of polyalphaolefin. The anti-oxidation property of this complex was evaluated by DSC and oxidation corrosion (OC) test. The OC test measured the oxidation stability of oil including the TAN and viscosity increase while incipient oxidation time (IOT) and the oxidation induction time (OIT) were measured by DSC. After combining MC with DODPA, the IOT and OIT of PAO were improved. The additives hardly exhibited the anti-oxidation properties in comparison with base fluids in OC test but their blend showed reduction of about 32.4 % in viscosity change. The DODPA containing lubricants showed larger TAN increase about 25.4 % as compared with base fluids. In POA mixture on both MC and DODPA exhibited good inhibition against deposits, a good synergism was found between MC and DODPA as clear from the results. In the oxidation



of PAO, the changes occurring in DODPA with and without MC were analyzed by GCMS. Finally, the anti-oxidation synergism was proposed for MC with DODPA [117].

Okoye *et al.* evaluated the anti-oxidation effect of quercetin on the oxidation stability of lubricating and base oil. The physico-chemical parameters used to assess the thermo-oxidative stability of oil samples under study were kinematic viscosity (at 40 °C and 100 °C); total acid number and the pH. The results obtained showed improvements in the thermal and oxidation stability of the formulated lube oil. Both the base oil and the formulated oil, showed similar patterns of degradation as temperature of the reaction increased. However, the formulated oil found to be more resistant than the base oil under the conditions studied [118].

Eissa *et al.* evaluated the oxidation stability of lubricating oil in the presence and absence of antioxidants. Oxidative stability was investigated by using physico-chemical tests (K.V, TAN and CR) and FTIR analysis. Inhibitor used was non ionic surfactant, alkanoamide which resulted in the improvement of oxidative stability. The lubricant used having the B. P range of 280-400 °C and its physico-chemical properties were determined using standard ASTM/IP methods. Structural group analysis was also performed to observe the compositional changes before and after oxidation by FTIR and refractive index-density –molecular weight methods [119].

Kreivaitis *et al.* reported that many of the mineral lubricants used in the world today contribute much in causing environmental pollution. To decline pollution, environmentally friendly lubricants may be encouraged to use. The attractive base oil for environmentally friendly lubricants is vegetable oil. However, it has some disadvantages like poor oxidation stability. In the current research, the influence of thermal oxidation on physico-chemical, and environmental properties of rapeseed oil was reported. Spectral analysis, viscosity and viscosity index were used. The rapeseed oil (RO) was oxidized for 20 h and 40 h and their induction period was determined using Rancimat 743 method. The oxidative stability of oil was assessed in terms of above physico-chemical properties. The results showed the oxidation stability in terms of OIT order original RO [20 h oxidized RO] 40 h oxidized RO [120].



Rahimi *et al.* evaluated the physico-chemical parameters of a mineral-based gasoline engine oil monitored at 0, 500, 1000, 2000, 3500, 6000, 8500, and 11500 kilometer of operation. Experimental results were obtained using inductively coupled plasma and some other techniques. The physico-chemical properties such as viscosity at 40 and 100°C, viscosity index, flash point, pour point, specific gravity,color, total acid/ base numbers and water content have been analyzed. The results revealed that the oxidative degradation could be attributed to the oxidation time or milage. Increase in viscosity at 40 °C and TAN and decrease in viscosity at 100°C and viscosity index values with mileage indicated the undertaking of undesired degradation [121].

Singh *et al.* investigated a blend of fractions of different paraffins as an industrial base oil which was heated to 130 °C in ambient and used as lubricant on steel disk sliding experiments in a steel pin in the presence and absence of test antioxidant; dimethyl disulfide (DMDS. FTIR monitored the primary and secondary products over a 100 h period of time. While at the pin surfaces, chemical transformation was monitored by XPS and friction plus wear of steel pin was measured for the same period. The focus of this work was to observe the catalytic action of steel component on aging process of oil and the proficiency of antioxidant to decline the oxidation of oil under test. For the process of aging, the possible mechanistic explanations and its impact on friction wear is also reported [122].

Rios *et al.* performed the synthesis, characterization and thermo-oxidative stability of alkyl phenol (5-n-Pentadecyl-2-tertbutyl phenol AP) as antioxidant in pure and blended form with mineral lubricating oil. AP synthesis was made with alkylation of hydrogenated cardanol the structure of which was confirmed by FTIR, NMR and GC-MS analyses. Thermo-analytical techniques such as TGA, DTG, DTA and DSC were employed for thermo-oxidative stability of mineral lubricating oil with and without AP as antioxidant. The AP doped mineral lube oil and non- doped lube oil samples were subjected to the aerated oxidation test according to modified method ASTM-2440. Blending of 1% AP as antioxidant in the lube oil samples reduced the oxidation peak areas carbonyl and peroxide:1.00-1.00 (in absence of AP) and 0.35-0.32, ROOH; 0.53-0.59 Cd0 (in presence of AP), respectively. The results revealed that AP reduced the formation of oxidized



products significantly in the lube oil sample. TGA analysis gave the integral procedure decomposition temperature (IPDT) for the AP (IPDT 268 C) higher than resulted for BHT (IPDT 163 C) indicated the larger thermal stability of AP than commercial BHT. All the thermo-analytical techniques exhibited good correlation [123].

Blaine *et al.* highlighted the effect of experimental conditions which were applied to hydrocarbons oil, vegetable oil, fats, grease and plastics. OIT is very sensitive to a number of experimental conditions such as temperature, flow rate of O₂, OIT onset determination, mass of sample and surface area of DSC thermogram. Inverse relation was found between temperature rise and OIT value (ASTM-E0698). OIT found was 40, 35 and 29 min at temperatures of 198, 200 and 202 °C, respectively. Most common method for OIT onset determination is drawing of tangent to the point of maximum rate of oxidation and to the base line prior to oxidation. OIT is the point where intersection of these lines occurred. The optimum flow rate of O₂ is 50 mL/min having pressure of 3.4 MPa was found for the precise and reproducible results. Decrease in flow rate usually increases the OIT (Ashy et al). OIT found 20.15 min at 0.1 MPa and 7.54 min at 3.4 MPa. The most precise mass sample required is of <5 mg. More use of sample shielded the sample from the reactive O₂ gas which markedly caused a change in OIT values. Moreover, increase in mass sample, increased the area of DSC thermogram lead to the broadening of peak (ASTM D5483). To get the best precision, experimental conditions must be maintained within narrow range of experimental conditions. Under carefully such controlled conditions, repeatability as good as 4.5 min and reproducibility as good as 8.7 min may be obtained [124].

After going through the detailed literature review, it can be inferred that most of the previous work is devoted to the use of antioxidants for inhibiting the undesired thermo-oxidative degradation. The results obtained in the most of the studies are promising in term of preventing degree of degradation in the presence of antioxidants. However, due to high cost of synthetic commercial antioxidants, and their environmental risks, the natural antioxidants are preferred to be blended in the lubricant for the formulation of engine oil.



The present work aimed to avoid thermo-oxidative degradation of the base oil in the presence of biomass derived extracts as antioxidants. Rice husk and saw dust alcoholic extracts were used as antioxidants. The influence of a number of experimental conditions such as temperature, time, and concentration of each antioxidant was studied. The efficiency of the derived bio mass extracts at low and high temperatures is reported.

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CHAPTER # 2

EXPERIMENTAL



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2.1. SAMPLE COLLECTION

Mineral base oil (Group-III) was collected from Hydrocarbon Development Institute, Peshawar Operation. Physico-chemical properties of the oil sample under study were determined according to standard ASTM/IP designated methods. Biomass samples of rice husk and saw dust were collected from local market. Methanol (Merck) was used as solvent.

2.2. EXTRACTION OF BIOMASS

Each of the biomass samples was soaked in an appropriate amount (5 L kg⁻¹) of methanol as a solvent in a vat for 72 hrs. The solution was then decanted and rota vapoured to collect the extract. The antioxidant activity of each of the extract was determined by 2, 2-diphenyl-1-picryl-hydrazyl radical (DPPH) radical method.

2.2.1. Antioxidant Activity of Biomass Extracts

The antioxidant activity of extracts was determined by using DPPH method reported in the literature [1]. In a typical procedure, DPPH solution was prepared by dissolving 0.0025 g in 100 mL of spectroscopic grade methanol. Then, the solutions of the crude extract in methanol were prepared in different concentrations i.e. 20, 40, 60, 80, 100 µg/L. An aliquot (0.5 mL) of MeOH extract was taken in a spectroscopic cuvette (quartz), to which 3.9 mL of DPPH solution was added, mixed well and left to stand at room temperature till stabilization. The absorbance of the resultant solution (upon stabilization) was measured at 515 nm using a double-beam UV-Vis spectrophotometer (Schimadzu-160) against a blank (MeOH extract without DPPH). The % inhibition of DPPH radical was calculated using the following equation:

$$\% \text{ Inhibition/radical scavenging activity (RSA)} = 100 \times \left(\frac{A_0 - A_{\text{sample}}}{A_0} \right)$$

Where:

A_0 : The absorbance measured in case of the blank (control)

A_{sample} : The absorbance measured in case of the test sample.

2.3 OXIDATION STUDY

2.3.1. Procedure

Oxidative degradation study of the oil under study was performed using a sample tube made of borosilicate glass provided with a vent head for air and oil introduction and gas outflow using modified method IP 48 [2]. An aliquot of 50 ml of the oil sample was summed up in to the tube. The tube was immersed in a heater and installed with an angle of 90° between the experimental set-up and the floor. Once the reactor has been filled with the sample, and assembled, the bath was heated using a heater to the desired oil temperature. A thermocouple was used to monitor the temperature during the course of the experiment. A suction pump was used to purge the reactor and maintain a constant flow of the air. The oxidation was studied under a flowing stream of air. Air was provided at flow rate of $10 \text{ L h}^{-1} 50 \text{ g}^{-1}$. The oxidation was performed at low and elevated temperatures. After termination of each experiment, the residual oil was decanted from the reactor and stored for further analysis. A schematic of the experimental setup is given in Fig.2.1. The experimental matrix includes the effect of reaction temperature, time and concentration of the antioxidants.

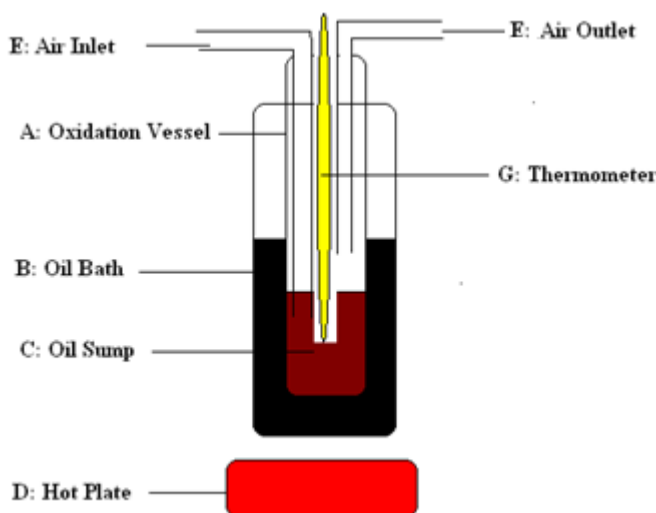


Fig.2.1. Schematic sketch of the experimental set up



2.3.2. Effect of Oxidation Temperature and Time

In this set of experiments, the oil was oxidized at different temperatures that are 25, 100, 150 and 200°C, for different time durations that are 00, 6, 12, 18 and 24 h, separately. The residual sample from each step was collected and stored for further analysis. Optimum temperature and time were decided from the percent changes in physico- chemical properties of the oxidized oil in comparison with the control.

2.3.3. Effect of Antioxidants Concentration

In this set of experiments, the concentration of each of the anti oxidants was varied between 0- 3% and the oxidation was performed at optimum temperatures and time. The residual sample from each step was collected and stored for further analysis. Optimum concentration was decided from the percent changes in physico-chemical properties of the oxidized oil in comparison with the control.

2.4 CHARACTERIZATION OF ORIGINAL AND OXIDIZED LUBRICATING OIL SAMPLES

As allowed by IP-48 standard method, the degradation of oil was evaluated by determining the physico-chemical properties according to ASTM standard test methods [3] which include principal properties i.e. kinematic viscosity at 40°C, ASTM D445, kinematic viscosity at 100°C, viscosity index, ASTM D2270 and viscosity ratio ASTM D445/IP 71. Complementary analyses of fresh and oxidized oils carried out were; Conradson carbon residue ASTM D189, acid number ASTM D664 and iodine number ASTM D1959.

2.4.1. Physico-chemical Analysis

2.4.1.1 Determination of Kinematic Viscosity (ASTM D 445)

The capillary tube viscometer method described in ASTM D445 (ISO 3104) was modified and automated using automatic viscometer (Stanhope Seta Kinematic viscometer, UK). The bath of the apparatus was filled with paraffin oil as bath liquid. A precleaned & well dried thermometer which can record in °C was hung in to the bath. The viscometer



withwide capillary (large “C”) among the various viscometers mounted in the bath was selected. The sample was heated and filtered through a disc filter paper made of polythene. Desired amount of the sample (0.4 ml) was put in to the viscometer and allowed to flow under its own weight. The meniscus of the flowing oil was carefully observed and the time of flow of the sample through the capillary of the viscometer between two red circles marked as A and B on the viscometer was noted.

Kinematic viscosity (v) was calculated as:

$$V = C \times t$$

Where

V = Kinematic viscosity in mm^2/s .

C = Viscometer’s calibration constant in $\text{mm}^2/\text{s/s}$.

T = Time elapsed in flow of sample from point A to B in seconds.

2.4.1.2. Determination of Viscosity Index (ASTM D2270-82)

Viscosity index was calculated using V.I calculator using the previous data of kinematic viscosities determined at 40 °C (100 °F) and 100 °C (212 °F).

2.4.1.3. Determination of Oxidation Tests/ Stability Factor/ Viscosity Ratio (ASTM D445 IP 71)

The viscosity ratio was reported as:

$$\text{Viscosity increase} = [(B-A)/A] \times 100$$

Where:

A = Kinematic viscosity at 40 °C of fresh oil

B = Kinematic viscosity at 40 °C of oxidized oil.



2.4.1.4. Determination of Carbon Residue (ASTM-D189-81)

The equipment used consisted of a large porcelain crucible placed inside two iron crucibles and heated by a gas burner until all petroleum vapors are driven off. A known weight of oil (10 g) was placed inside the porcelain crucible, and the apparatus was assembled accordingly and heated at such a rate to ensure burning of vapors within about 10 min. The flame was then adjusted in order to burn the sample for a further 21-23 min. The crucibles were then heated to a cherry-red heat for a further 7-8 min, giving a total time of approximately 30 min. The crucible containing the carbonaceous residue was cooled in a desiccator and weighed. This residue was subsequently oxidized to an ash by heating in a muffle furnace at 750 °C allowed to cool, and weighed. The amount of residue was corrected for the ash content and reported as the Conradson carbon residue (CCR).

2.4.1.5. Determination of Total Acid Number (TAN) (ASTM D 974 and ASTM D 664)

Five gram oil sample was dissolved in 50 mL of toluene and shaken it well to get clear sample solution. A 50 ml aliquot of neutralized alcohol was added to the sample solution. The sample solution containing 2-3 drops of Phenolphthalein was titrated against 0.1 N alcoholic KOH solution and the Total Acid Number (TAN) or total acidity was determined as mg KOH/g of sample.

$$\text{Total Acidity Number (mg KOH/g)} = \frac{56.1 \times V \times N}{W_t}$$

Where:

56.1 = Equivalent weight of KOH.

V = Volume of Alcoholic KOH used.

N = Normality of Alcoholic KOH.

W_t = Weight of sample taken.

2.4.1. 6. Determination of Iodine Number (IN) (ASTM D5554 – 95)

About 20 gram of MBO was taken in a well dried conical flask. Carbon tetrachloride as solvent (about 20 ml) was added to the flask and then shaken until the sample was completely dissolved. To the flask contents 25 ml of the iodine solution was



added through pipette. The mixture of flask was mixed very well by shaking and allowed to stand in the dark for 120 minute kept at a temperature of 20°C. After the completion of reaction period 20 ml of the potassium iodide was added to the flask containing sample, CCl₄ and iodine solution. The content of the flask was shaken until complete mixing was achieved. Excess of the iodine was titrated against the sodium thiosulphate solution using starch as indicator. Same procedure was repeated for the blank without sample, using same reagents with same amounts. Blank was allowed to stand and kept for same length of time at dark and at same temperature. Iodine number was reported in milligram of the iodine used per gram of the sample as mg/g.

$$IN = \frac{12.7 \times N \times (B-A)}{W_t}$$

Where:

IN = Iodine Number.

N = Normality of thiosulphate solution.

B=Volume of thiosulphate solution in ml used for blank

A=Volume of thiosulphate solution in ml used for the sample

W_t = Weight of sample taken

2.4.1.7. Calculation of Derived Parameters

Calculations of percent changes and number of times changes for the determination of significant changes between original MBO and variously oxidized (un-additized, RHE-additized and SDE-additized) MBO samples carried out. These calculations were made for all types of like physico-chemical, spectroscopic, thermo-analytical and calorimetric under study using below given equations.

% Change in various parameters like kinematic viscosity at 40 °C, viscosity ratio, Conradson carbon residue, total acid number and iodine number was calculated by following equation (Eq. 1).

$$\% \text{ Change} = \frac{P_v - O_v}{O_v} \times 100 \dots\dots\dots (1)$$

Where,

P_v =Value of parameter for the oxidized un-additized or additized base oil



O_v = Value of parameter for the original base oil

In case of some parameters such as kinematic viscosity at 100 °C and viscosity index, the % change was determined through equation (Eq. 2) below.

$$\% \text{ Change} = \frac{O_v - P_v}{O_v} \times 100 \dots\dots\dots (2)$$

Similarly number of times difference for some parameters like TAN & IN (physico-chemical analysis phase II) and Peak area increase and peak height (FTIR analysis phase III) was determined by using the following equation (Eq. 3).

$$\text{No. of Times Difference} = \frac{P_v - O_v}{O_v} \dots\dots\dots (3)$$

2.4.2. Spectroscopic Analysis

2.4.2.1. Fourier Transform Infra Red (FTIR) Spectrophotometric Study (ASTM D2412)

A double beam FTIR spectrophotometer model Shimadzu FTIR-820.1 PC was used in this study. Firstly, potassium bromide (KBr) pellets were prepared using extra pure powdered KBr. Spectrum of one of the KBr pellet was taken, as a reference. A small drop of test oil was spread on the already prepared KBr disc. Absorbance of the test oil was noted in the wave number range of 4000-400 cm⁻¹. The spectral resolution of 02 cm⁻¹ was used and the average of 03 scans were taken for FTIR analysis.

2.4.2.2. UV/Visible Analysis

The antioxidant activity of RHE and SDE was determined using UV/visible spectrophotometer (Model Shimadzu 160 A). An aliquot of each sample was diluted in five ml of n- hexane taken in quartz cell of diameter of 1cm and spectrum for each sample was obtained against the blank.

2.4.3. Oxidative Stability Index (OSI) by Rancimat Method (EN-14112/IS-15607)

Rancimat method [4] was followed to measure the OSI time. In a typical procedure, 3 g of the oil sample was taken in the oxidation assembly. The assembly was heated in the temperature range of 50-200 °C. During oxidation, air was continuously passed at a rate of 120 mL/min. Volatile products of oxidation were transferred with air current to a vessel containing 50 mL of de-ionized water where these were absorbed. The vessel was provided with conductance or pH probe that furnished increase in conductance in milli-Siemens (ms) or decrease in pH due to presence of degradation ions. The conductance or pH change was measured continuously until rapid change observed. The time of oxidation at this abrupt change was noted as oxidative induction time or oxidative stability index time (OSI time). In order to exactly calculate the OSI time, the results of increase in oxidation time vs conductance/pH were plotted to get oxidograph and the point at which abrupt increase is observed was noted as OSI.

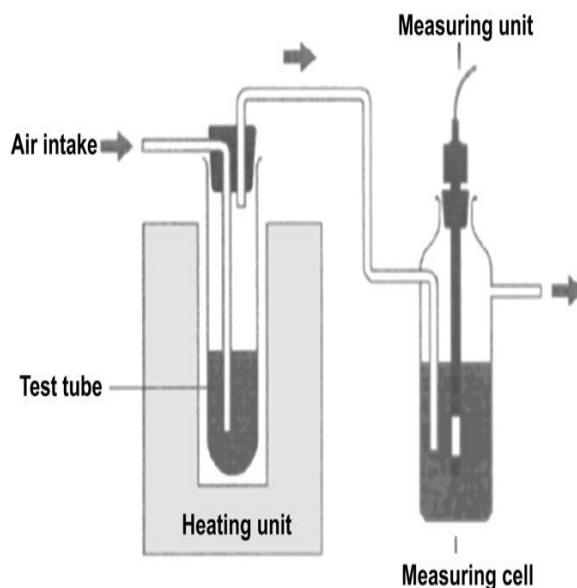


Fig.2.2. Measurement of the OSI time using Rancimat test method (EN-14112/IS-15607)



2.4.4. Thermogravimetric Analysis (Programmed TGA)

Thermogravimetric analysis was carried out using TGA analyzer Model (TGA/SDT 85e Mettler Toledo-Switzerland). Samples were heated at a rate of 10 °C min⁻¹ under O₂ and N₂ atmospheres at (50 ml min⁻¹) from ambient to 700°C.

2.4.5. Pressure Differential Scanning Calorimetric Analysis (Isothermal PDSC)

Pressure differential scanning calorimeter equipped with a pressure cell PDSC, model No (DSC 823e Mettler Toledo-Switzerland) was used. Thermo-balance was used under O₂ environment with temperature ramp 10 °C min⁻¹ from ambient till the establishment isothermal temperature of 100 or 200°C. Before analysis, the instrument was calibrated. A weighed amount of the test sample was taken in an open aluminum pan. The PDSC cell was flushed with oxygen to remove the air and then pressurized up to 1800 kPa. The temperature was adjusted and the experiment was started. The isothermal conditions were chosen to provide reasonable isotherms with time taken (5-75 min) at two different temperatures.

2.4.6. GC-MS Analysis

GC-MS analysis of RHE, SDE, original oil, and variously oxidized oil samples was carried out by gas chromatograph coupled with MS analyzer (Model GCMS-QP2010, Shimadzu, Japan). The chromatograms were developed under the given standard conditions:

Conditions	Level
Column	DB-5MS (25 m x 0.25 mm i.d, 0.25 µm)
Carrier gas	Helium (AR. grade)
Injector	Auto injector (ADC-201).
Split ratio	50
Sample injection volume (µl)	1
Flow rate of carrier gas (ml/min)	1.3
Injector temperature (°C)	300
The initial oven temperature (°C)	35



During the analysis, the initial oven temperatures was increased to 100 °C with heating rate of 5 °C min⁻¹ and hold time of 5 min, further increased to 150 °C with ramp of 10 °C min⁻¹ and hold time of 10 min. Finally the temperature increased to 290 °C at the rate of 2.5 °C min⁻¹ with an isothermal held of 10 min. The product peaks in the chromatogram were identified by NIST MS library.

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CHAPTER # 3

RESULTS AND DISCUSSION



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Oil is exposed to oxygen/air at elevated temperatures in the engine which may degrade the quality of oil. Various commercial additives are added to inhibit this degradation. In recent years, the role of laboratory methods in evaluating the effectiveness of engine oil additives has dramatically enhanced, especially in predicting the efficiency of engine oils under field test conditions. In the present study, the oxidation stability of the mineral base oil samples with and without antioxidants was evaluated in an air atmosphere using temperature and time ramped oxidation. The antioxidants used were derived from the wood biomass (saw dust, SD) and the non- wood biomass (rice husk, RH). The alcoholic extracts of the rice husk (RHE) and the saw dust (SDE) were obtained. The oxidative stabilities of the mineral base oil (MBO), the base oil blended with RHE, and the base oil blended with SDE were evaluated at different temperatures and times using modified IP 48 procedure. The study was carried out in several phases.

Phase-1: In this phase, the feed sample that is MBO, RH and SD were characterized by the well established ASTM/IP designated methods. The biomass derived extracts i.e. RHE and the SDE were analyzed for their antioxidant properties by DPPH radical scavenging method.

Phase-II: In this phase, the un-additized, the RHE-and SDE-additized base oil samples were subjected to air oxidation at different temperatures and for different oxidation times. The extent of degradation was estimated from changes in the physical and chemical properties of the residual oil in comparison to the un-oxidized original oil. Principal physico-chemical properties such as kinematic viscosity (ν or KV) determined at 40 & 100 °C, viscosity index (VI) & viscosity ratio (VR) and complementary properties such as Conradson carbon residue (CCR), total acidity number(TAN) & iodine number (IN) were determined using standard ASTM Methods (Table.3.1). Optimum temperatures and time of oxidation on the basis of the significant changes in these properties were decided.

Phase-III: Oxidation may lead to formation of carbonyl compounds (carboxylic acids or esters) leading to changes in the spectroscopic properties of the oil. In order to know



about the chemical changes occurring in the base oil during oxidation, FTIR analysis of the original oil, and un-additized MBO, RHE- & SDE-additized samples oxidized at optimum temperatures and time was performed in order to identify the oxidation products like carboxylic acids/carboxylates, amides, esters, etc.

Phase IV: In this set of experiments, the conductance changes occurring in the oil samples during oxidation were recorded in order to decide about the oxidation induction times (OIT) and oxidative stability index (OSI). The changes were measured in case of the un-additized and RHE- & SDE-additized base oil samples oxidized at 100 and 200 °C for time duration of 06 h.

Phase V: Next to OSI analysis, the thermo gravimetric analysis (TGA) were performed in case of the un-additized and various additized base oil samples oxidized at 100 and 200 °C for time duration of 06 h in order to evaluate their thermal stabilities in terms of T_{onset} , T_{offset} , mass loss and weight gain.

Phase VI: Calorimetric analyses in terms of oxidation induction time (OIT) were performed in case of the oil samples spiked with biomass derived extracts in comparison to un-additized MBO in order to evaluate the antioxidant character of the RHE and SDE.

Phase VII: To decide about changes in spectroscopic properties of the original and variously oxidized residual oil samples, Gas chromatographic- Mass spectrometric analysis was carried out in order to ascertain the changes in the individual compounds, the hydrocarbon range products and the hydrocarbon group type's distributions.

The results are presented in the proceeding sections.

**Table: 3.1.Standard ASTM Test Methods Used**

Property	Unit	Test method
Density @ 15 °C	g/cm ³	IP160/87/ ASTM D-2598
API gravity @ 60°F	-	IP160/87/ ASTM D-1298
Ash	% wt	IP 4/81/ASTM D-482-80
Kinematic Viscosity @ 40°C	mm ² /s	IP 71/80/ ASTM D-445-74
Kinematic Viscosity@ 100°C	mm ² /s	(ASTM D 445)
Viscosity Index	-	(ASTM D2270-82)
Viscosity Ratio	-	(ASTM D445/ IP 71)
Total Acidity Number (TAN)	mg KOH/g	(ASTM D974, D644)]
Carbon Residue	% wt	IP13/82/ASTM D-189-88
Iodine Number	mg/g	ASTM D- 1959
Flash Point	(°C)	IP 15/67/ ASTM D-97
Cloud Point	(°C)	IP 15/67/ ASTM D-97
Pour Point (°C)	(°C)	IP 15/67/ ASTM D-97



PHASE-1

In this phase, the feed samples (MBO, RH and SD) were characterized by following the well established ASTM/IP designated methods. The biomass derived oils i.e. RHE and the SDE were analyzed for their antioxidant properties by following the DPPH radical scavenging method. The results are presented in the subsequent section.

3.1. CHARACTERIZATION OF MBO, RHE AND SDE

3.1.1. Characterization of MBO

Characterization of the MBO was carried out. Physico-chemical properties like density (ρ), specific gravity, API gravity, ash, Conradson Carbon Residue (CCR), kinematic viscosity, both at 40 and 100°C (ν), viscosity index (V.I), cloud point, pour point, Total Acid Number (TAN), Total Base Number (TBN), and Iodine Number (IN) were determined. The results are provided in Table 3.2. All properties are in agreement with the standard specifications [1-5].

3.1.2. Characterization of Rice Husk & Saw Dust and Their Alcoholic Extracts

3.1.2.1. Physico-chemical Properties

The raw rice husk (RH) & saw dusts (SD) were characterized. The RH and SD samples were well ground and sieved to particle size of about 0.15-0.45 mm. The proximate analyses were performed using ASTM standard methods. The results are provided in Table 3.3 which showed that the RH and SD have 1.20 & 1.60 % moisture, 65.50 & 68.25 % volatile matter, 1.16 & 2.23 % fixed carbon and 1.16 & 2.33 % ash, respectively.

The ultimate analysis were also performed which indicate that the RH and SD contained 42.75 & 38.44 % carbon, 5.15 & 4.98 % hydrogen, 0.40 & 0.45 % nitrogen and 38.95 & 36.84 % oxygen, respectively. The data is in conformity with the results reported by other researchers [6-9].

**Table: 3.2.Physico-chemical Properties of Base Oil**

Parameter	Unit	Value
Density @ 15 °C	g/cm ³	0.89
API gravity @ 60 °F	-	35.50
Ash	wt%	0.13
Kinematic viscosity @ 40°C	mm ² /s	110
Kinematic Viscosity @ 100°C	mm ² /s	15.50
Viscosity Index		150.2
Viscosity Ratio		1.00
Conradson carbon residue	wt %	0.20
Total Acid Number	mg KOH/g	0.40
Iodine number	mg/g	17
Flash point	°C	244
Pour point	°C	-25

**Table: 3.3. Proximate and Ultimate Analysis of Rice Husk and Saw Dust**

Analysis (wt %)		RH	SD
Proximate analysis (ASTM D 3173-75)			
Moisture	(ASTM D 3173)	1.20	1.60
Volatile matter	(ASTM D 3173)	65.50	68.25
Ash	(ASTM D 3174)	1.16	2.33
Fixed Carbon	(ASTM D 3172 – 89)	17.11	15.14
Carbon residue	(ASTM D 189)	18.27	17.47
Ultimate analysis			
Carbon		42.75	38.44
Hydrogen		5.15	4.98
Nitrogen		0.40	0.45
Oxygen		38.95	36.84

3.1.2.2. Antioxidant Activities of RHE and SDE by DPPH Method

The antioxidant activities of the RHE and SDE were determined once by UV-VIS spectroscopy using DPPH scavenging assay. The results are given in Table 3.4 which showed a linear relationship between the concentrations of the antioxidant in the extracts versus DPPH. Out of the two samples tested, the RHE showed the % inhibition of 43.3, 53.33, 91.16, 92.16, 92.03 and 92.51 at 20, 40, 60, 80, and 100 µg/L, respectively while the SDE showed 35.11, 46.77, 70.12, 80.86 and 81.41 at 20, 40, 60, 80, and 100 µg/L, respectively. The higher % inhibition (% RSA) indicates a higher antioxidant activity. Among the different concentrations of the extracts used, 100 µg/L gave the highest % RSA in case of both the RHE and the SDE. Among the two crude extracts, RHE showed better antioxidant behavior compared to SDE. The variation can be corresponded to the different chemical composition in terms of phenolics and aminincs.

The use of DPPH free radical is more beneficial in investigating the antioxidant activity attributed to its larger stability than hydroxyl and super oxide [10, 11]. DPPH is a stable free radical possessing maximum absorption at 517 nm that receive an electron or



hydrogen atom to become a stable diamagnetic molecule. The free radical nature of DPPH is lost in the presence of substance capable of donating the proton (antioxidant) and hence the decrease in the DPPH absorption at 517 nm was observed revealed its reduction in concentration. Moreover, the abstraction of proton from antioxidant molecule caused the conversion of violet DPPH methanol solution color to yellow diamagnetic product. Reduction in the concentration of DPPH indicated the larger amount of antioxidant in the extract as observed in case of RHE and SDE extracts under test. Concentration of the RHE and SDE was found to be the function of DPPH concentration. Fresh DPPH methanol solution gave deep purple color which became fade when treated with the RHE and SDE containing antioxidants. This transformation was measured spectrophotometrically and the disappearance of purple color was monitored at 517 nm. For the optimum concentration of the RHE and SDE (100 µg/ml), the DPPH concentration used was found to be 92.51 % for RHE and 81.41 % for SDE as given in Table 3.4. The results reflected the higher antioxidant activity of the RHE than SDE because reduction in DPPH concentration was found to be significant in case of RHE than SDE. The higher antioxidant capacity of the RHE compared to SDE may be due to the high concentration of phenolic contents in RHE [12, 13].

Table 3.4. Antioxidant Activity Data of RH and SD by DPPH Method

RHE		SDE	
Concentration (µg/ml)	Antioxidant activity (%)	Concentration (µg/ml)	Antioxidant activity (%)
20	43.3	20	35.11
40	53.33	40	46.77
60	91.16	60	70.12
80	92.03	80	80.86
100	92.51	100	81.41



PHASE-II

In this phase, the un-additized, the RHE-and SDE-additized base oil samples were subjected to air oxidation at different temperatures and different oxidation times. The extent of degradation was estimated from the changes in the physical and chemical properties of the residual oil in comparison to the un-oxidized original oil. Optimum temperatures and time of oxidation were decided on the basis of the significant changes in these properties. The results are presented and discussed in the proceeding section.

3.2. OXIDATIVE DEGRADATION STUDY

The influence of the antioxidants under study on the oxidative stability of the base oil was studied. For this purpose, the MBO samples in un-additized and additized forms were subjected to low and high temperature oxidation performed for different time intervals. The RHE and SDE were used in different concentrations i.e. 1, 2 and 3 %. Low temperature oxidation (LTO) was carried out at 25 & 100 °C and high temperature oxidation (HTO) at 150 and 200 °C. The oxidation was carried out in time cycles of 06 h that is 06, 12, 18 and 24 h in LTO and HTO. Degradation of the MBO was assessed by the changes in physical and chemical properties termed as physico-chemical markers [14]. These markers are KV at 40 °C, KV at 100 °C, VI, VR, TAN, CCR and IN. Among these, KV at 40 °C and at 100 °C, VI and VR are principal physico-chemical marker while TAN, CCR and IN are complementary physico-chemical markers. These markers or parameters are considered as tools for monitoring the oxidative stability of a lubricant. No single marker that can be looked at to assess when an oil is no longer usable for engine or industrial machinery. However, the laboratories of the oil analysis focus on combination of few markers to evaluate the status of the oil degradation by comparing residual oil values with standard original oil. In oil industries, importance is assigned to individual marker determination as well as with its permissible limit or range to which it undergo a change. The general limits used by oil analysis laboratories include TAN range from 4-7 mgKOH/g, viscosity change from 20- 50 % and DSC oxidation induction time range from 2-5 minutes [15- 17].

In the current study, changes in these markers were investigated in case of the original and various un-additized & additized MBO samples oxidized at different



temperatures and times in order to establish the role of antioxidants under study in avoiding the thermo-oxidative degradation.

3.2.1. Oxidative Stability Study of MBO in Absence and Presence of the Antioxidants

3.2.1.1. Effect of Air Oxidation on Physico-chemical Properties of the Un-additized Base Oil

In order to study the influence of temperature, the oxidation experiments were performed at low and high temperatures. In case of LTO, two temperatures were selected i.e. 25 and 100 °C. Similarly, in case of HTO, 150 and 200 °C were selected. Further, the effect of oxidation time was also studied.

In order to study the effect of oxidation time on the oil degradation, the un-additized MBO was oxidized for different time durations, separately. Oxidation time was kept variable between 0-24h and the oxidation was performed in time cycles of 06, 12, 18 and 24 h.

Air oxidation of the un-additized base oil was performed at different temperature i.e. 25, 100, 150 and 200 °C for different time durations, separately. The influence of temperature and extension in the oxidation times was studied on the change in kinematic viscosity characteristics was determined. The results are compiled in Figs 3.1- 3.4 which indicate a significant change in KV determined at 40 and 100 °C in case of the various oxidized samples compared with the control sample (110 C.st at 40°C and 15.50 C.st at 100°C) [17].

The results revealed onset of degradation performed at 25°C which pronounced further and attained significant changes with the increase in temperature from 25 °C to 100, then to 150 and finally to 200 °C which can be attributed to the fact that at low temperature, in the presence of oxygen some reactions like formation of low molecular weight acids occur [18]. These acids may cause sludge formation which in turn cause an increase in the KV. The generation of the acidic compounds may deplete the basicity of the oil and exacerbate the reactions particularly of polymeric components present in the



oil which can produce high molecular weight materials [17]. Viscosity variation may be related to the polymerization followed by precipitation of the oxidized products as earlier reported [18]. Another reason can be thought is the formation of hydrogen bonding and dipole–dipole interactions. As a consequence, higher intermolecular forces are formed, which increase the lubricant viscosity [19].

The degradation at high temperature may proceed via C-C bond scissions leading to sludge formation as reported earlier [19]. The change in viscosity observed in current investigation is quite pronounced at 200 °C compared to 100 °C. This is attributed due to the fact that for further changes in viscosity, secondary reactions are responsible, which require high temperatures [20]. Furthermore, organic species in mineral oils and lubricants are subjected to degradation by oxidation, especially at elevated temperatures and in the presence of air as oxidant. Such deterioration (degradation) often leads to buildup of insoluble carbonaceous deposits or sludge thus leading to increase in viscosity [21, 22]. The oxidation may generate hydroxyl groups in the matrix and thereby enhancing greater intermolecular packing and molecular cohesion, giving rise to higher resistance to shear and hence higher viscosity [23]. The oxidized hydrocarbons have an increased polarity which makes the lubricant more viscous.

Upon comparing the influence of time, it can be observed that the increase is enroute when the time was extended from 06 to 24 h in 06 cycles. However, this increase is quite significant in time cycle of 00-06 h compared to the extended time cycles i.e. 06-12, 12-18, and 18-24 h.

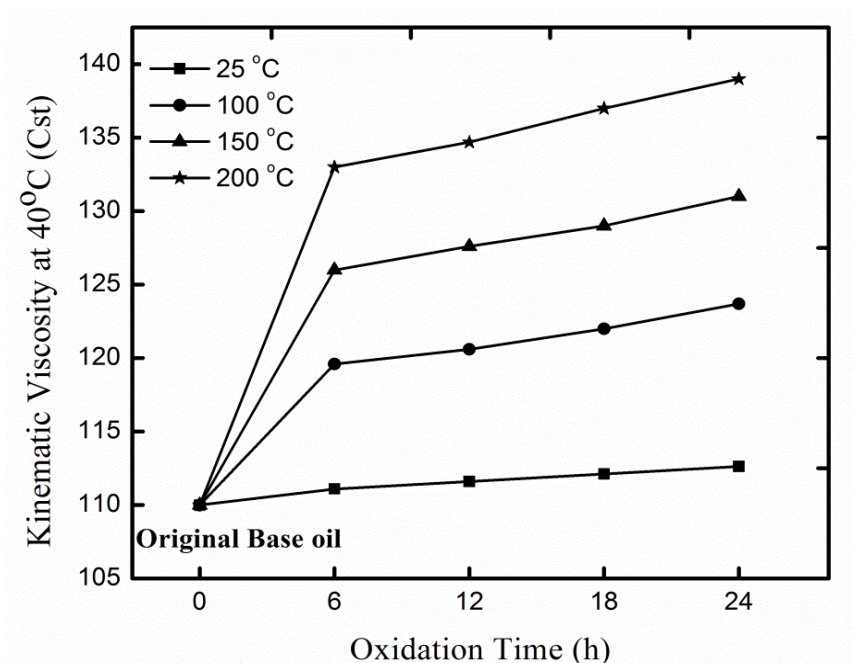


Fig.3.1. Kinematic viscosity (determined at 40 °C) of the original and oxidized base oil samples as a function of oxidation time and temperature

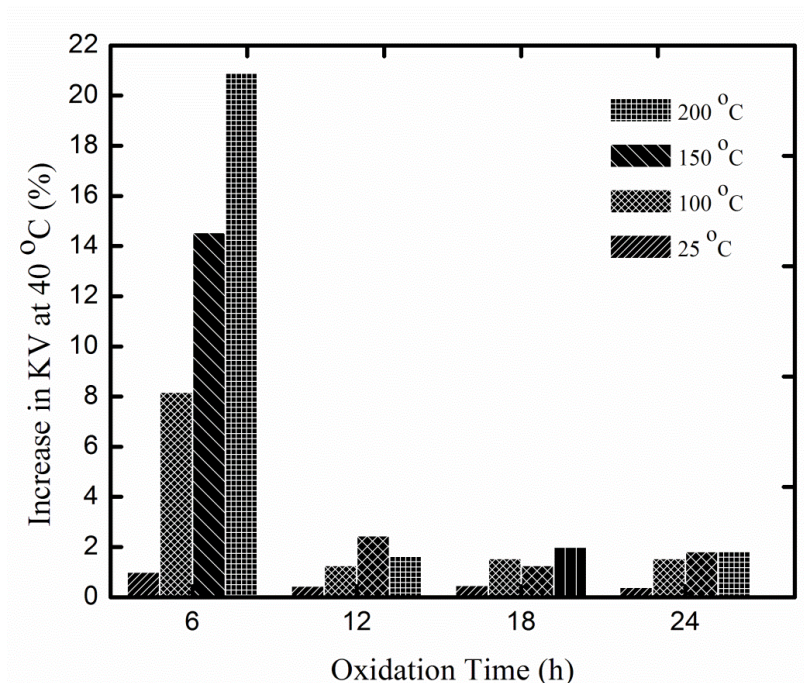


Fig.3.2. Percent change in kinematic viscosity relative to original oil (determined at 40°C) of various oxidized base oil samples as a function of oxidation time and temperature

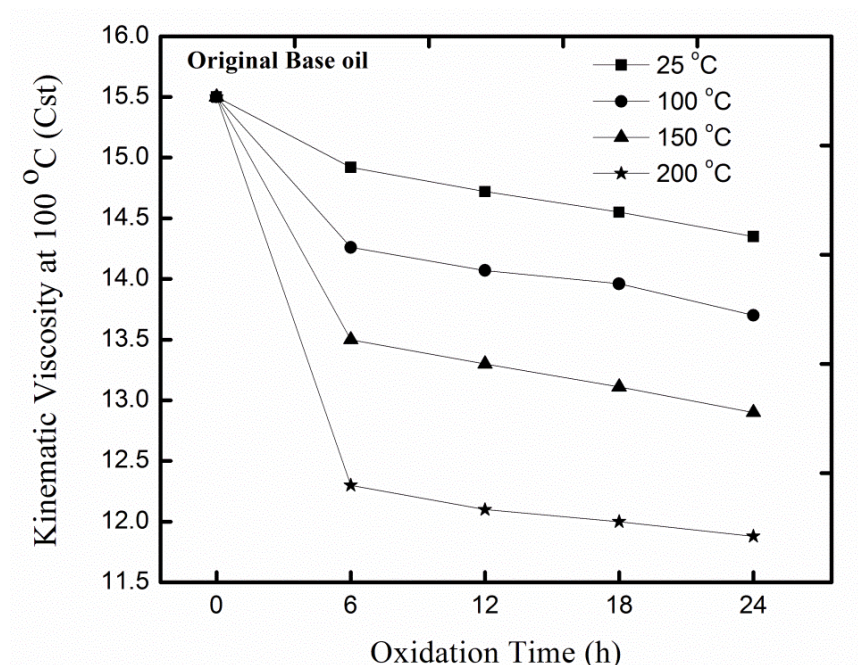


Fig.3.3. Kinematic viscosity (determined at 100 °C) of the original and various oxidized base oil samples as a function of oxidation time and temperature

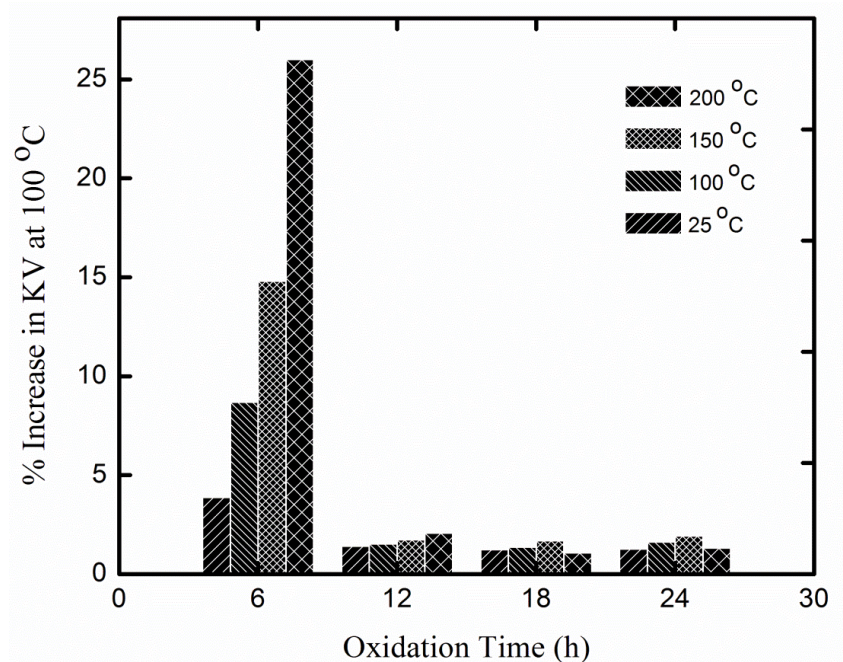


Fig.3.4. Percent change in kinematic viscosity relative to original oil (determined at 100 °C) of the various oxidized base oil samples as a function of oxidation time and temperature



The change in other viscosity characteristics i.e. VI and VR were also studied. The corresponding results are provided in Fig. 3.5-Fig.3.8, respectively. The high VI indicates that the oil is free from reactive hydrocarbons and other impurities that contribute to the degradation of oil in service [24]. High VI means that there is no significant change in viscosity with respect to increase in temperature. An oil of good quality must have viscosity of more than 4 C.st at 100 °C and VI of more than 100 [25]. It is also reported elsewhere that a change of VI during a high temperature oxidation is caused by a thermal stability of the viscosity modifiers rather than by oxidative ageing of oil [15].

It can be observed from the compiled results that the viscosity index of each oxidized oil sample was found to be decreased compared with that of the original oil. The VR values of the oxidized samples in comparison to the control are also plotted in the same Figs. It can be seen that all the values are higher than a unit value which revealed that oxidation has occurred which caused deterioration in quality of the oil under study.

The overall results of the viscosity characteristics indicate that the MBO samples undergone degradation in case of oxidation performed at different temperatures and for different oxidation times which can be corresponded to the fact that the base oil under study contains no additives and cannot withstand degradation effectively even at low temperature [26- 28]. The change in these properties are significant in the beginning of oxidation i.e. 0-06 h while in case of the oxidation performed for time duration beyond 06 h, i.e. 6-12 h, 12-18 h and 18-24 h, there is a gradual increase in ν , decrease in VI and increase in VR values which indicate that the oxidation is en-route but not so profound as in case of the oxidation performed in time cycle of 00-06 h.

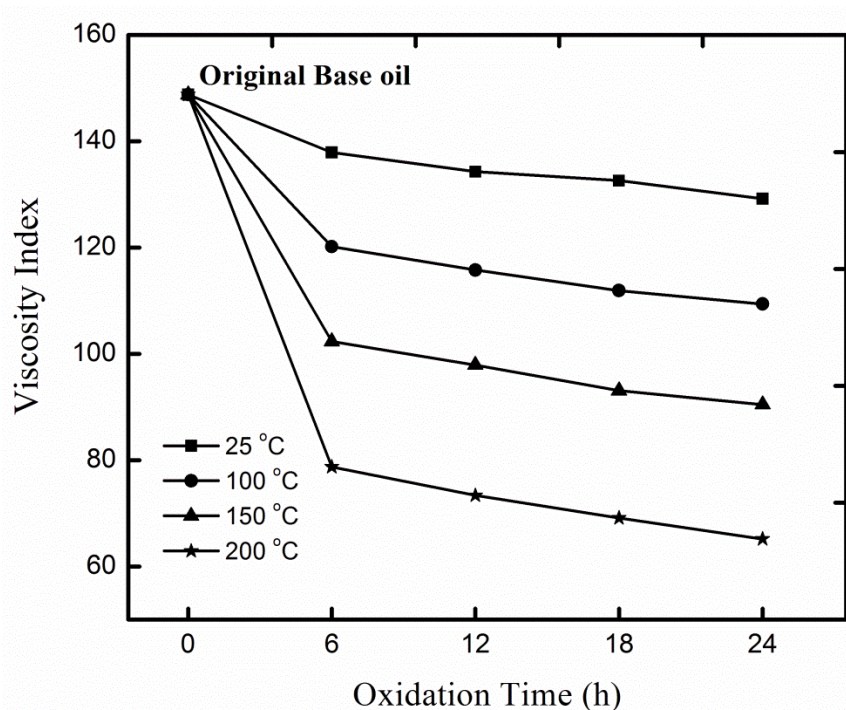


Fig.3.5. Viscosity index of the original and various oxidized base oil samples as a function of oxidation time and temperature

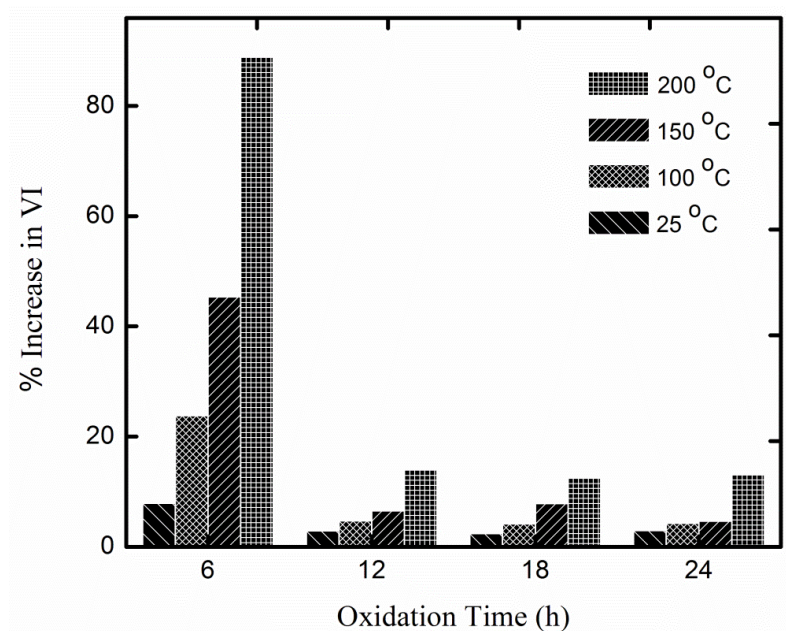


Fig.3.6. Percent change in viscosity index of the various oxidized base oil samples relative to original oil as a function of oxidation time and temperature

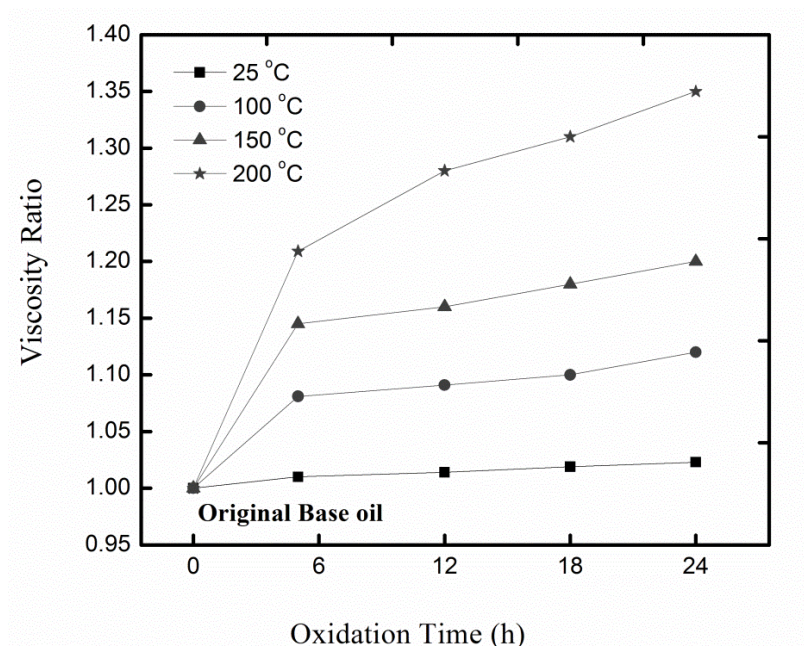


Fig.3.7. Viscosity ratio of the original and the various oxidized base oil samples as a function of oxidation time and temperature

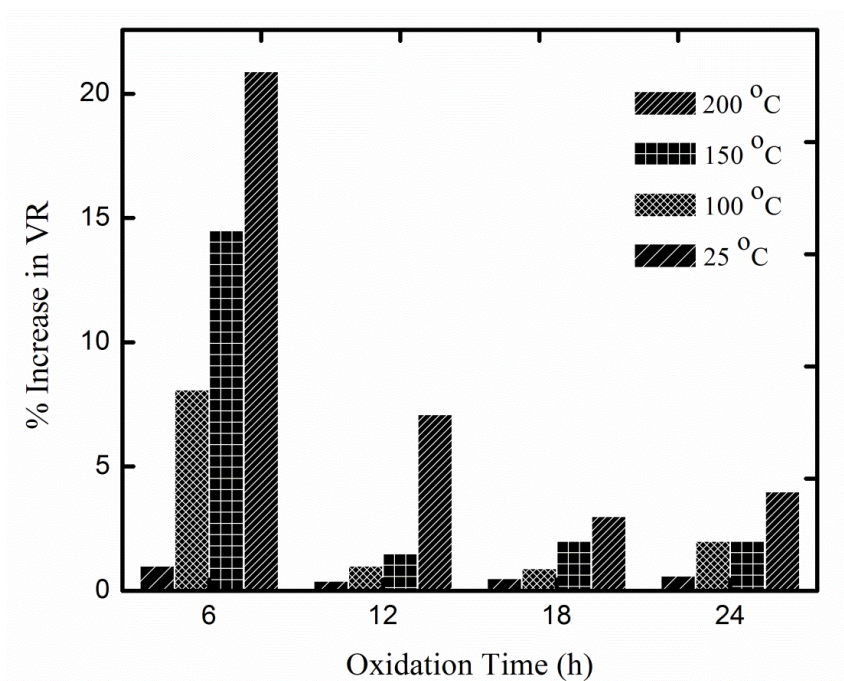


Fig.3.8. Percent change in viscosity ratio of the various oxidized base oil samples relative to original oil as a function of oxidation time and temperature



In order to ascertain the influence of time and temperature on the oxidative stability of the MBO understudy, complementary properties like CCR, TAN and IN were also determined which can be used as markers of oxidation [29]. The results have been compiled in Fig.3.9-Fig.3.14 which showed a noticeable change in all such properties as a function of oxidation time & temperature.

Carbon residue is the amount of carbon formed by combustion, oxidation and thermal degradation of lubricating oil. The test is used to calculate how much residue is left as a result of oxidative or thermal degradation. Actually, CR is the coked material in percent that left after the exposure of the lubricant to high temperature environment. Carbon residue is caused due to, oxidation, thermal degradation, additives, entrained air flow and aromatics contents of lubricants. CR if greater than 20 %, then it is problematic and cause serious damages including fouling of engine parts, filter plugging, oil passages & vehicular plus machinery valves. As reported elsewhere, the increase in CR is much larger at higher temperatures which may be due to insoluble contaminants due to pronounced oxidation [30] and more soot formation [31].

The influence of temperature and time on the CCR was studied. The results are given in Fig. 3.9 & Fig. 3.10 which indicated that the amount of CCR after oxidation is quite high reflecting the thermal oxidation changes in the residual oil samples particularly at elevated temperatures. The high carbon residue is most likely associated with the amount of aromatics and other carbon forming compounds as oxidation products. The high values of CCR at high temperatures indicate the formation of aromatics through dehydrogenation reactions.

Carbon residue is undesired due to the reason that it affect the performance of the lubricating oil [32]. It has several drawbacks including deposition on the walls of the container there by affecting the heat transfer. It also clogs the minute apertures and thus inhibits the mass transfer resulting in significant reductions in lubricant performance. Moreover, it may cause an increase in the viscosity with undesirable effects on the properties of lubricating oil.



Total Acid Number (TAN) is an analytical test which is used to determine the level of deterioration of a lubricant. The high value of total acidity (organic + inorganic) is mostly due to some organic acids formation. The organic acidity may be attributed to the generation of carboxylic (COOH), phenolic acid (PhOH) and carbonyl (CO) compounds. The results given in Fig. 3.11 & Fig.3.12 indicate that the TAN values were significantly increased with the increase in both oxidation temperature and time. High TAN indicates that the lubricant is more acidic and the degradation has proceeded [33]. The resultant acids dimerize or trimerize further in the presence of oxygen which subsequently polymerize to yield insoluble sludge [34].

The amount of olefins in lube oil sample is determined in terms of IN (mg/g). The results compiled in Fig. 3.13 & Fig.3.14 indicate an increase in IN values with the increase in oxidation temperature and time. The IN test in turn indicates oil disintegration. Low IN value is required for a good lubricant since less no of double bonds impart high oxidative stability. Olefins are undesired in lubricating oil owing to their detrimental effect on some properties of the lubricant. Un-saturation increases the low-temperature fluidity of oils by lowering their melting point, as these bonds form a “kink” in the structure. Further, this unsaturation does not allow the individual molecules to come closer to each other and this inhibit easy stacking due to a break in symmetry of the molecules, thereby resulting in the formation of micro rather than macro-crystalline structures. At lower temperatures, such microcrystalline structures can easily tumble and glide over one another resulting in better fluidity of the total matrix [35]. The results are in agreement with the change in viscosity determined at 100 °C.

Comparing the results of all of the physico-chemical properties determined in case of samples oxidized over a period of time, and at different temperatures, it can be observed that the changes in such properties are very pronounced at the beginning of oxidation when the time was extended from ambient to 06 h in case of both low and high temperatures oxidation compared to the oxidation performed in time cycles beyond 00-06 h. The results compiled also reveal that the oil under study is susceptible to oxidation at higher temperatures compared to low temperatures. This can be attributed to the evaporation losses of the volatile compounds formed at the beginning of the oxidation in



case of low temperature and due to the formation of the oxidized products involving C-C bond scissions in case of high temperature oxidation.

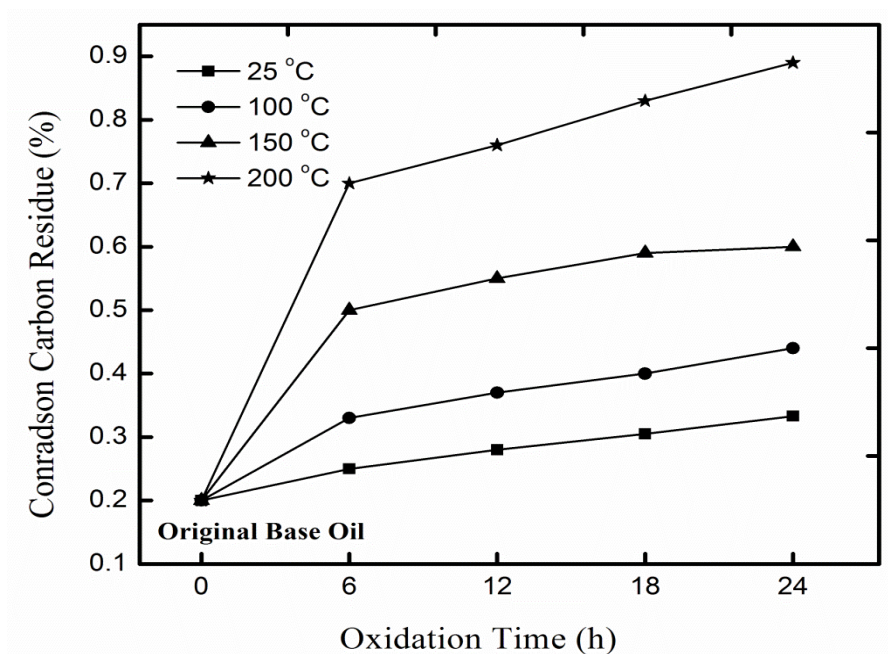


Fig.3.9. Conradson carbon residue of the various oxidized base oil samples as a function of oxidation time and temperature

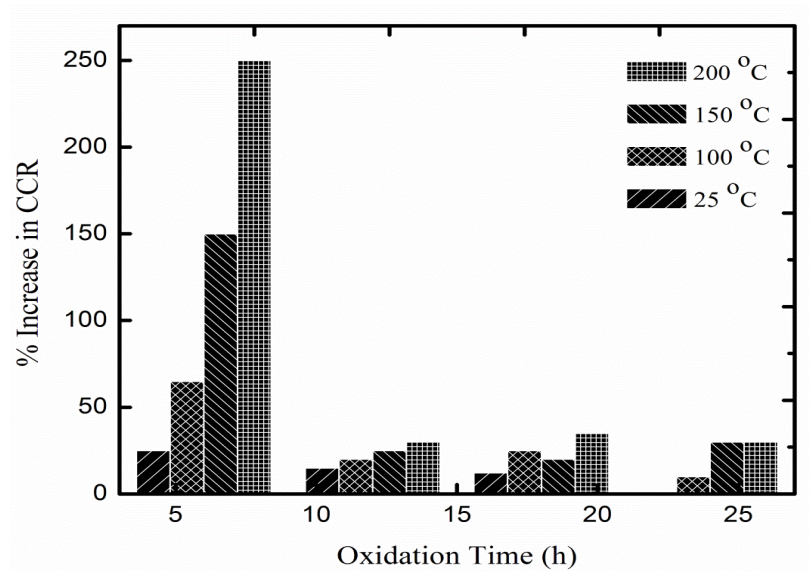


Fig.3.10. Percent change in Conradson carbon residue of the various oxidized base oil samples relative to original oil as a function of oxidation time and temperature

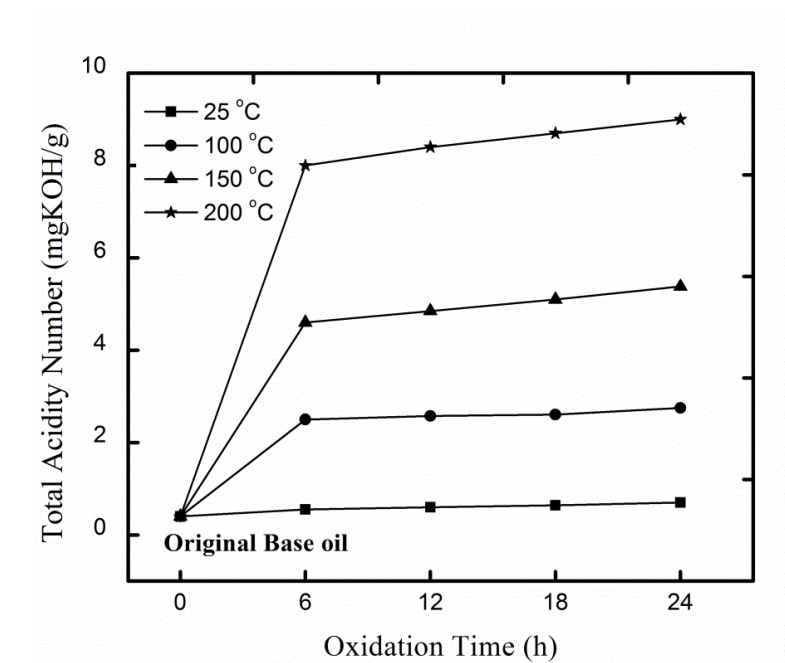


Fig.3.11. Total acid number of the original and various oxidized base oil samples as a function of oxidation time and temperature.

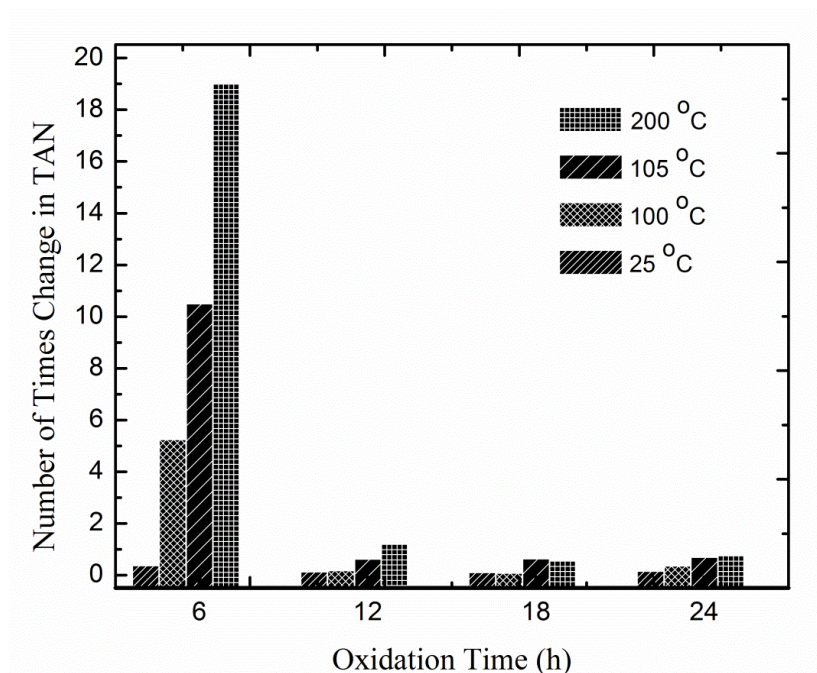


Fig.3.12. Number of Time change in total acid number of the various oxidized base oil samples relative to original oil as a function of oxidation time and temperature

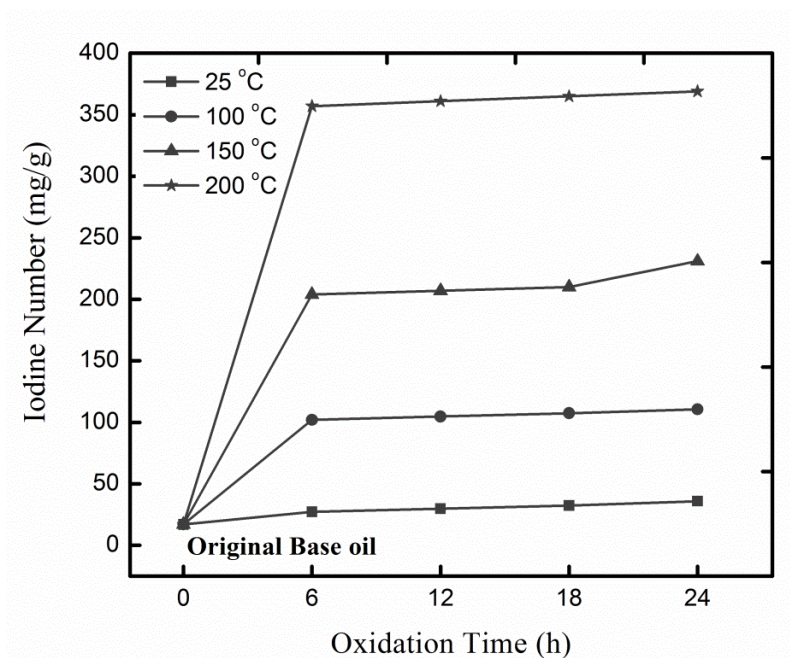


Fig.3.13. Iodine number of the original and various oxidized base oil samples as a function of oxidation time and temperature

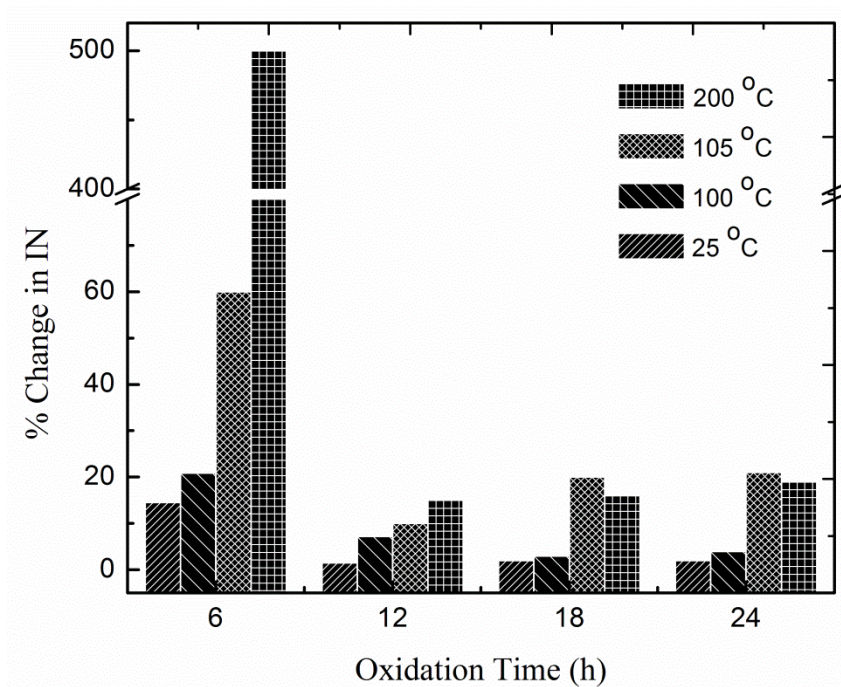


Fig.3.14. Percent change in iodine number of the various oxidized base oil samples relative to original oil as a function of oxidation time and temperature

It is concluded from the results obtained in case of both LTO and HTO, that the oil under study is susceptible to degradation and the extent of degradation appeared to be more profound in case of oxidation performed for 0-06h and elevated temperatures which can be attributed to formation of carbonyl compounds (carboxylic acids or esters) which in turn accelerate the rate of oxidation of the various components present in the base oil like aliphatics, aromatics, naphthenics, cycloaliphatics, olefins and iso-paraffinic [31].

Percent changes in viscosity characteristics and other complementary parameters were assessed in case of both LTO and HTO for optimization of the oxidation time and temperature for further study. The percent changes in viscosity characteristics and complementary properties indicate that the maximum oil was degraded in oxidation time interval of 00-6h followed by 12-18h, followed by 06-12h and followed by 18-24h at 100 °C in case of LTO and 200 °C in case of HTO. Keeping in view the significant changes in the physico-chemical properties, an optimum time for significant MBO degradation was found to be 06h [34]. Thus, rest of the study in case of e additized base oil samples was performed at 06h & 100°C in case of LTO and 06h & 200 °C in case of HTO.



3.2.1.2. Effect of Air Oxidation on the Physico-chemical Properties of the Base Oil Additized with Antioxidants

The antioxidants used in the current study were the RHE and SDE. It is well established that the base oil is more vulnerable to oxidation without the oxidation inhibition additives. Antioxidants are added alone or in synergistic combinations extend the operating life of the oil by improving its oxidation stability.

As depicted in the basic mechanism of oxidative degradation and the role of the different antioxidants, the oxidation begin with the formation of reactive compounds like free radicals, hydro peroxides and peroxides. Upon propagation, they give rise to the formation of oxygenated hydrocarbons, such as alcohol, acids and sludge. The oxidation is avoided by the antioxidant(s) by removing radicals (primary antioxidants) or by decomposing hydro peroxides to form non-reactive stable products (secondary antioxidants). Phenolics, phenates, salicylates and amine types are the most commonly used primary antioxidants. The secondary antioxidants used are usually sulfur or metal-containing additives.

The influence of both antioxidants (RHE & SDE) which are enriched in phenolics on the thermo-oxidative degradation of the MBO was studied. The results have been given and discussed in the proceeding section.

Effect of RHE and SDE

The oxidative stability of the MBO was determined by fortifying the samples with the antioxidants under study. Both antioxidants were used in different concentration (0, 1, 2 and 3 %) and the oxidation was performed at previously optimized temperatures (100 and 200 °C) and time (6h), separately. Parameters relating to oxidative stability as described above were determined for the variously oxidized/residual oil samples in comparison with the un-additized samples. The results are compiled in Fig. 3.15-Fig. 3.28.

The viscosity characteristics i.e. KV, VI and VR of the MBO samples i.e. RHE- and SDE-additized samples oxidized at 100 and 200 °C for time duration of 06h as a function of concentration of each antioxidant were studied. The results are given in Fig.

3.15-Fig.3.20. It can be seen that in case of LTO as well as HTO, the additized base oil samples exhibited quite significant differences in viscosity characteristics (Fig. 3.15 and Fig. 3.17). In case of RHE-additized samples, the changes indicate that oxidation has been significantly controlled as compared to the un-additized sample.

The percent changes in viscosity characteristics in comparison with the control were also determined in case of the RHE-and the SDE-additized MBO samples. The results are provided in Fig. 3.16 & Fig. 3.18 which indicate that as the concentration of the antioxidants is increased, the percent difference decreases which show the antioxidant characters of the RHE and SDE.

The influence of the antioxidants on other viscosity characteristics i.e. VI and VR was also studied. The results have been compiled in Figs. 3.19- Fig. 3.22. Upon comparing with results obtained in case of the un-additized MBO samples; the use of antioxidants caused to control the changes in all of these properties which in turn have confirmed their antioxidant character.

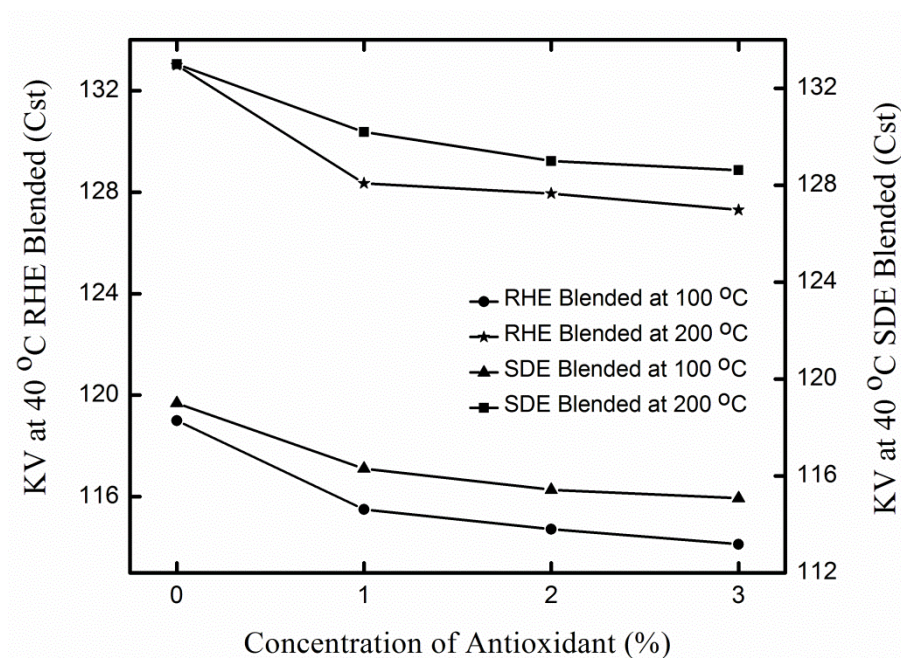


Fig.3.15. Kinematic viscosity (determined at 40 °C) of the additized base oil samples oxidized at 100 and 200 °C as a function of concentration of the antioxidants

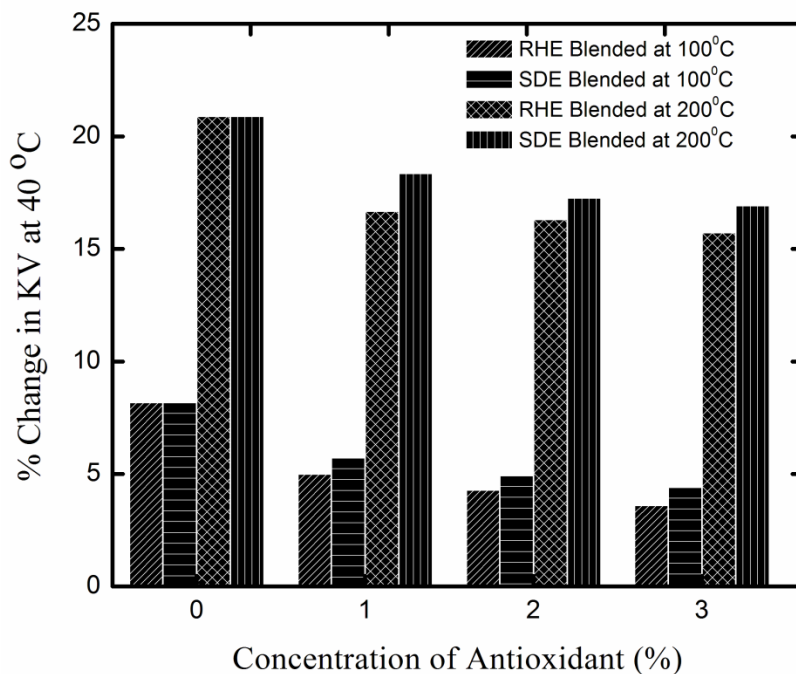


Fig.3.16. Percent change in kinematic viscosity (determined at 40 °C) of the additized base oil samples oxidized at 100 and 200 °C in comparison with control

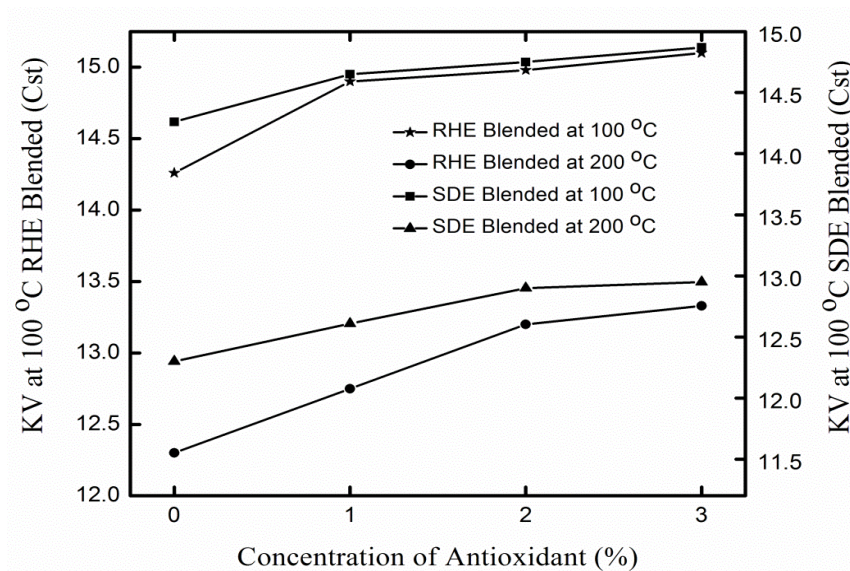


Fig.3.17. Kinematic viscosity data (determined at 100 °C) of various additized base oil samples oxidized at 100 and 200 °C as a function of concentration of the antioxidant

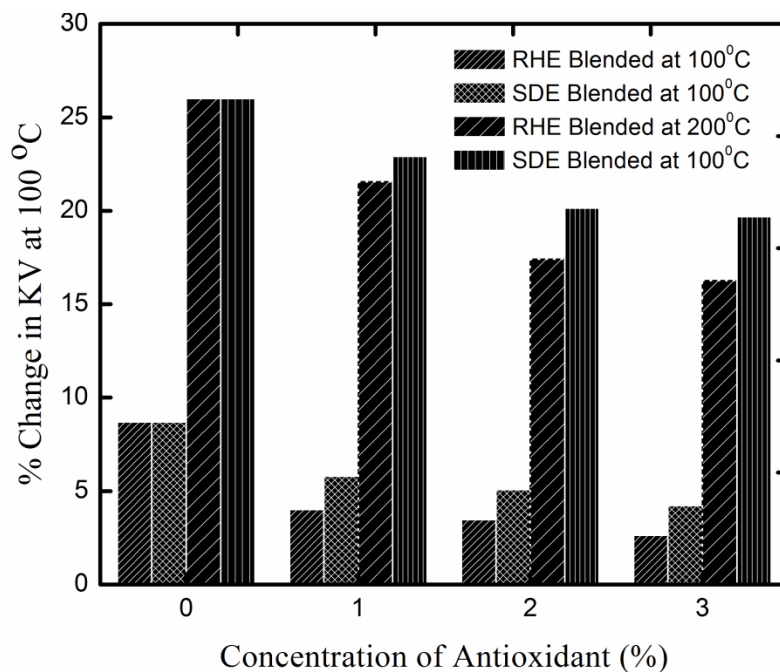


Fig.3.18. Percent change in kinematic viscosity (determined at 100 °C) of the various additized base oil samples oxidized at 100 and 200 °C in comparison with control

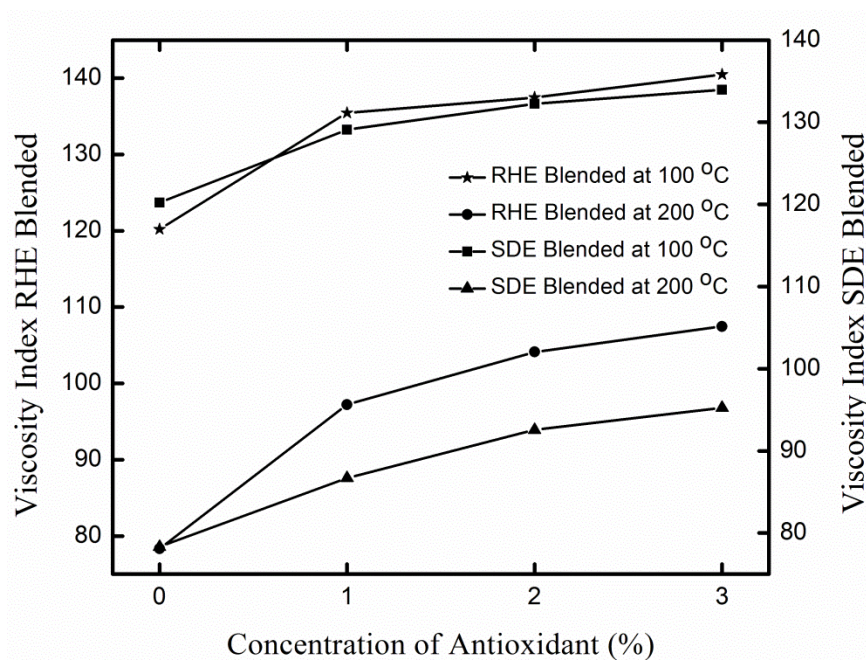


Fig.3.19. Viscosity Index of the various additized base oil samples oxidized at 100 and 200 °C as a function of concentration of the antioxidants

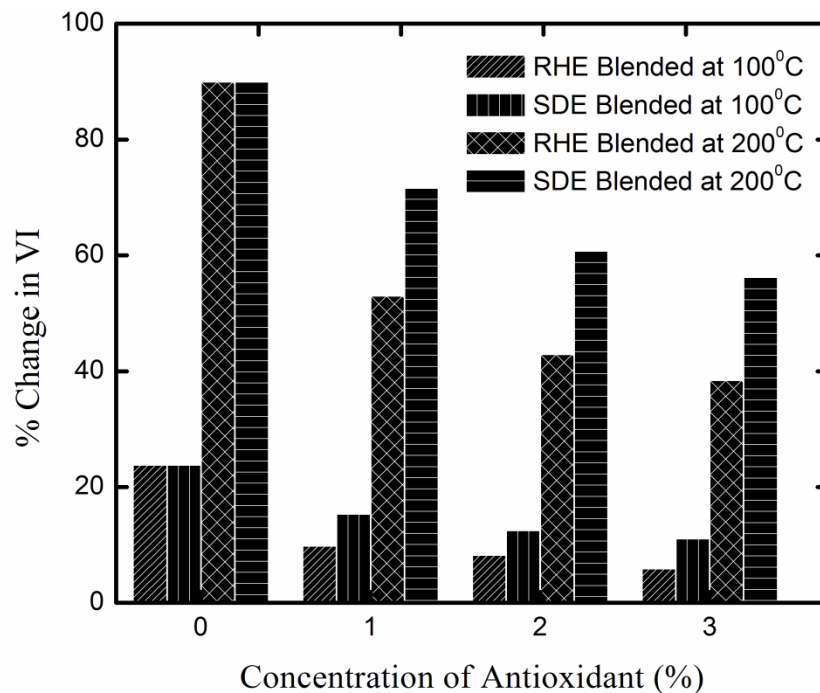


Fig.3.20. Percent change in viscosity index of the various additized base oil samples oxidized at 100 and 200 °C in comparison with control

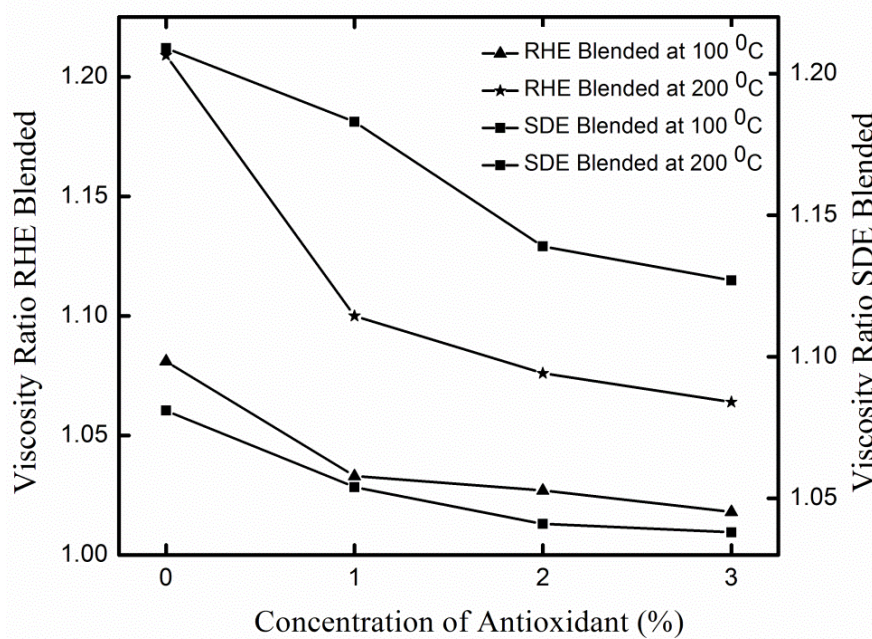


Fig.3.21. Viscosity ratio of the various additized base oil samples oxidized at 100 and 200 °C as a function of concentration of antioxidants

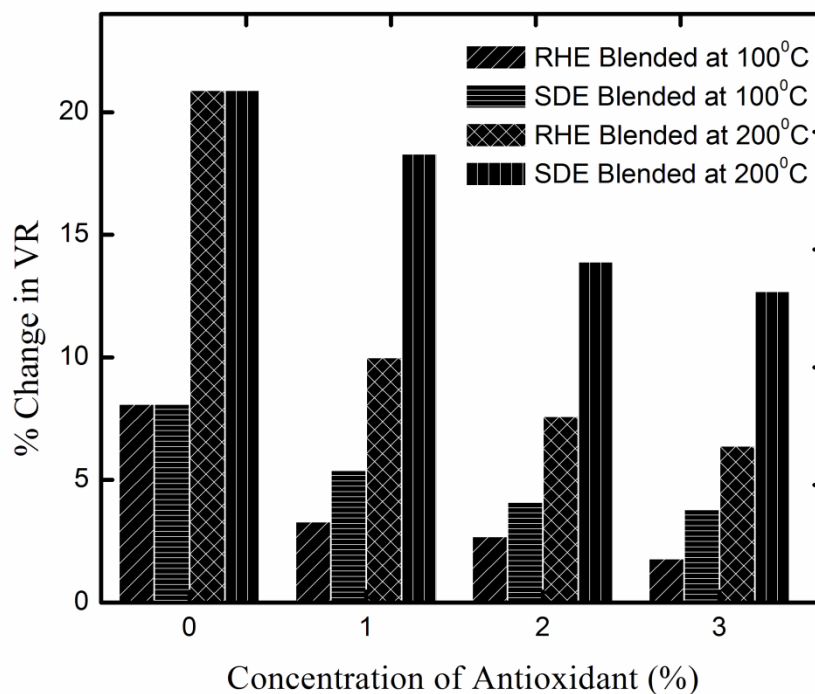


Fig.3.22. Percent change in viscosity ratio of the various additized base oil samples oxidized at 100 and 200 °C in comparison with control

The level of degradation was also evaluated from the complementary properties (CCR, TAN and IN). The results are compiled in Fig. 3.23-Fig.3.28. Upon comparing the results with the un-additized samples, it can be observed that the level of degradation has been reduced to a greater extent in the presence of antioxidants. The results further indicate that concentration of 3 % appeared to be the optimum in case of LTO as well as HTO.

It is inferred from the overall results that the use of RHE and SDE influenced the viscosity characteristics and the complementary properties which were improved significantly in comparison with the un-additized MBO indicating their antioxidant role in case of both LTO and HTO.

Upon comparing the efficiency of the two antioxidant used among themselves, overall antioxidants performance of RHE can be ranked as outstanding at 100 °C & excellent at 200 °C and SDE as excellent at 100 °C & better at 200 °C. It can be



concluded that these biomass derived antioxidants can be used in formulation of commercial lubricants.

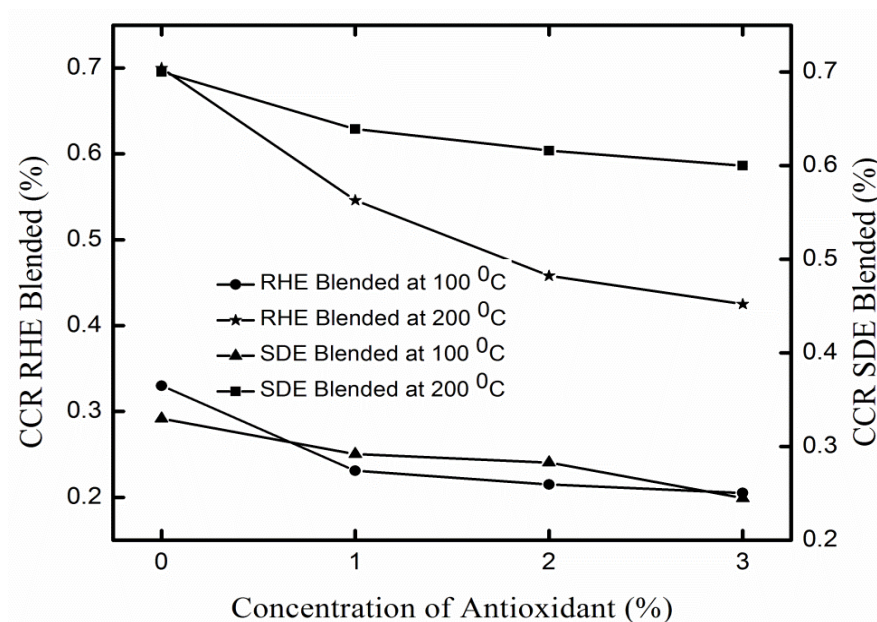


Fig.3.23. Conradson carbon residue of various additized base oil samples oxidized at 100 and 200 °C as a function of concentration of antioxidants

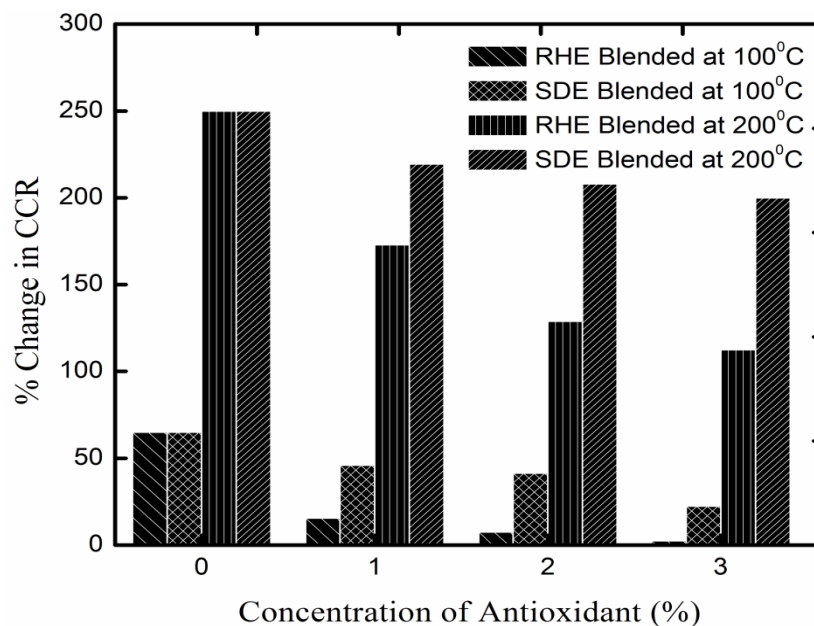


Fig.3.24: Percent change in Conradson carbon residue of the various additized base oil samples oxidized at 100 and 200 °C in comparison with control

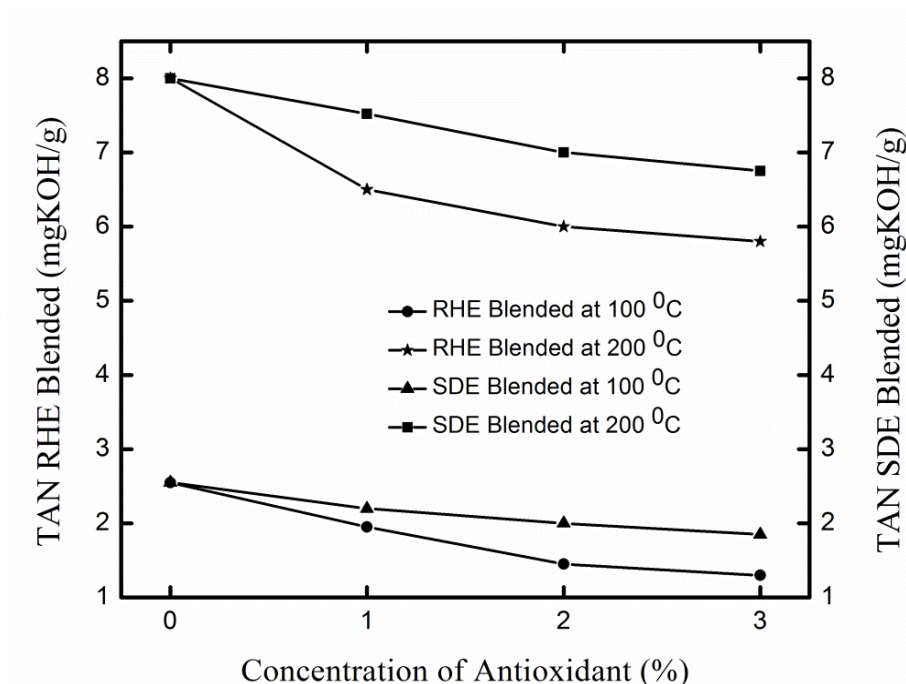


Fig.3.25. Total acid number of the various additized base oil samples oxidized at 100 and 200 °C as a function of concentration of antioxidants

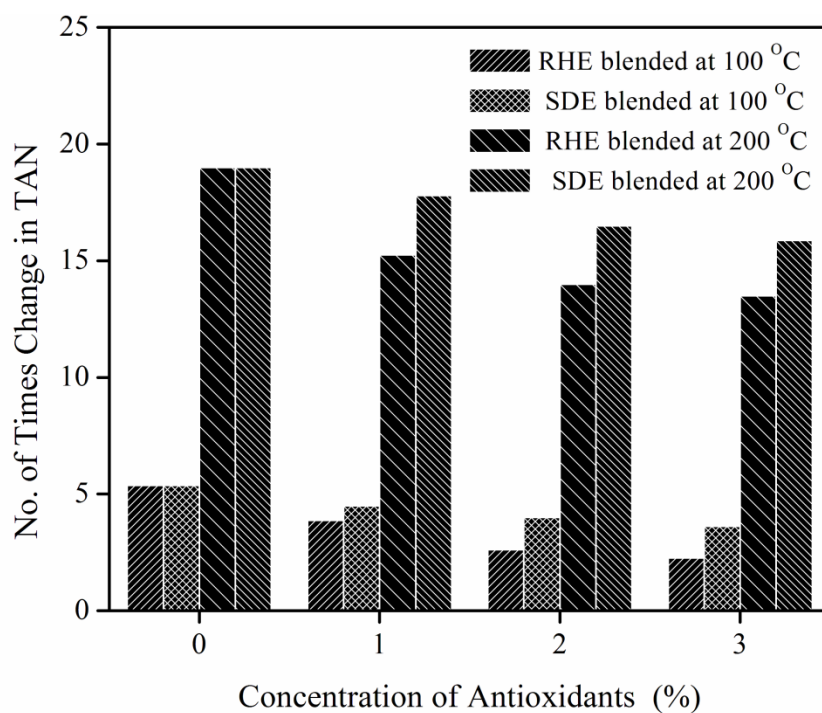


Fig.3.26. Number of time changes in total acid number of the various additized base oil samples oxidized at 100 and 200 °C in comparison with control

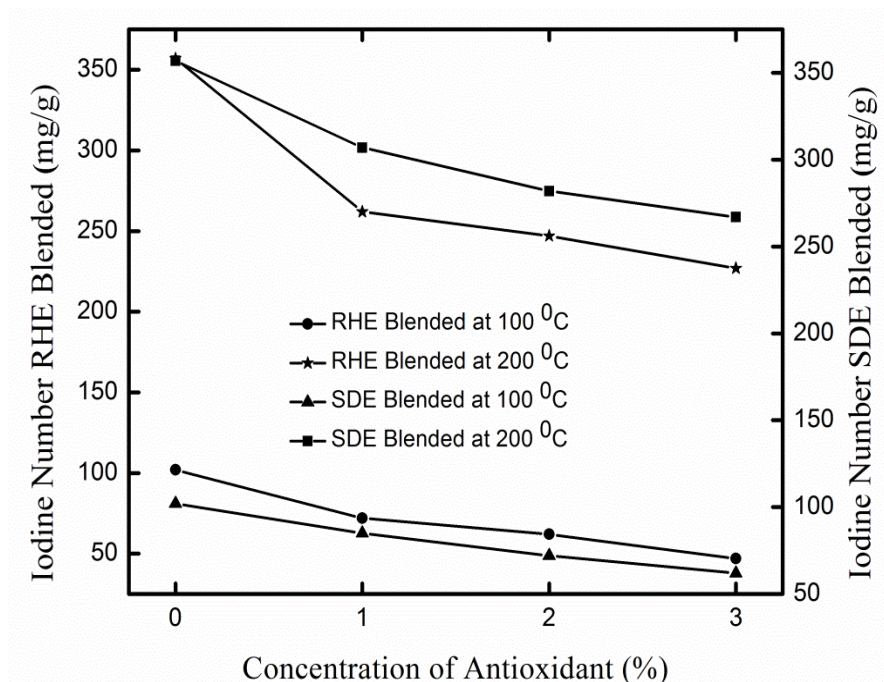


Fig.3.27. Iodine number of the various additized base oil samples oxidized at 100 and 200 °C as a function of concentration of antioxidants

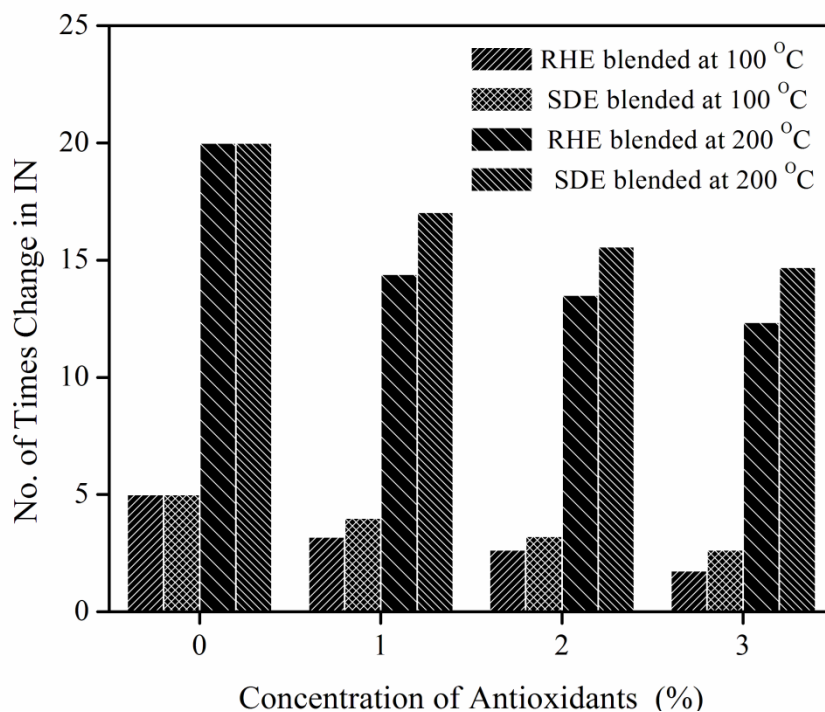


Fig.3.28. Number of time changes in iodine number of the various additized base oil samples oxidized at 100 and 200 °C in comparison with control



PHASE-III

Oxidation may lead to formation of carbonyl compounds (carboxylic acids or esters) leading to changes in the spectroscopic properties of the oil. In order to know about the chemical changes occurring in the base oil during oxidation and to identify the oxidation products like carboxylic acids/carboxylates, amides, esters, etc., FTIR analysis of the original oil, and un-additized MBO, RHE-and SDE-additized MBO samples oxidized at optimum temperatures for 6h was performed. The results are provided in the given sections.

3.3. COMPOSITIONAL ANALYSIS OF ORIGINAL AND VARIOUS OXIDIZED BASE OIL SAMPLES BY FTIR

FTIR analysis is conducted in order to measure the difference in the level of degradation of base oil [36, 37]. The level of degradation or oxidation is quantified by measuring the area under carbonyl (C=O) or double bond (C=C) bands in order to determine concentration of the oxidation products using Peak Area Increase (PAI) and Peak Height (PH) methods [ASTM 7214-07].

Peak area increase & peak height are employed as criterion for evaluating the level of degradation of lubricant. In this method, FTIR spectra of oil before and after air oxidation are taken in transmission mode in a cell of known path length. The spectra are then converted to absorption mode and spectrum of original oil is subtracted from the oxidized oil sample. This gave a resultant differential spectrum under which a base line is set in the spectral regions of 1500-1650 and 1651-1900 cm^{-1} . The areas between the base line and C=O group and C=C group are calculated with a software coupled with FTIR instrument. The area under C=O band is divided by the cell path length in millimeters and the obtained result is reported as PAI (PAI unit $\text{Abs cm}^{-1}/\text{mm}$). The PAI is representative quantity of all of the compounds containing C=O group (aldehydes, ketones, carboxylic acids, esters or anhydrides). The PAI reflects the quantitative information for a particular class of compound resulted from degradation due to oxidation.

In peak height (PH unit Abs) method, absorbance of original and oxidized oil is determined and then inter-compared. Absorbance of oxidized oil is usually much larger



than original oil and the corresponding difference give the level of degradation. The absorbance peak height of oxidized oil is compared with original oil that gives information about the extent to which oil under test is degraded quantitatively. Absorbance enhances with the increase in concentration of compounds possessing same functionality and thus Beer-Lambert law is followed. PAI and PH methods are also used for measurement of other peaks areas associated with specific family of compounds [38].

3.3.1. FTIR Analysis of RHE, SDE, Original (un-oxidized), and Various Oxidized Base Oil Samples

3.3.1.1. FTIR Analysis of RHE and SDE

The functional groups of RHE and SDE were analyzed through FTIR. The data are compiled in Table 3.5 while the corresponding spectra are shown in Fig.3.29 (a) & Fig.3.29 (b).

The spectra show a very large band centered at $3200-3600\text{ cm}^{-1}$ which can be corresponded to O-H and N-H stretching vibrations indicate the presence of phenols, alcohols and aromatic amines. A medium intensity peak appeared in the wave number range of $2850-3000\text{ cm}^{-1}$ which can be assigned to saturated C-H bending vibrations confirms the presence of alkanes. A well-developed band can be observed in the wave number range of $1600-1800\text{ cm}^{-1}$ which may be due to C=O stretching vibrations revealed the carbonyl compounds i.e. aldehydes, ketones, carboxylic acids and esters. A large band centered in the wave number range of $1500-1650\text{ cm}^{-1}$ can be corresponded to C=C stretching vibrations. Some medium intensity peaks in the range of $1100-1377\text{ cm}^{-1}$ can be observed which may be due to C-O stretching vibrations indicate the presence of alcohols or esters. An apparent peak centered in the range $822-970\text{ cm}^{-1}$ presents the C-H bending vibrations confirms the presence of aromatic hydrocarbons.

The results indicate the presence of various organic compounds in both RHE and SDE samples. Moreover, the area under the peaks appeared for phenols is large, intermediate for carbonyl compounds and small in case of peaks corresponded to the aromatic contents revealed their high, medium and low concentrations [39-41].

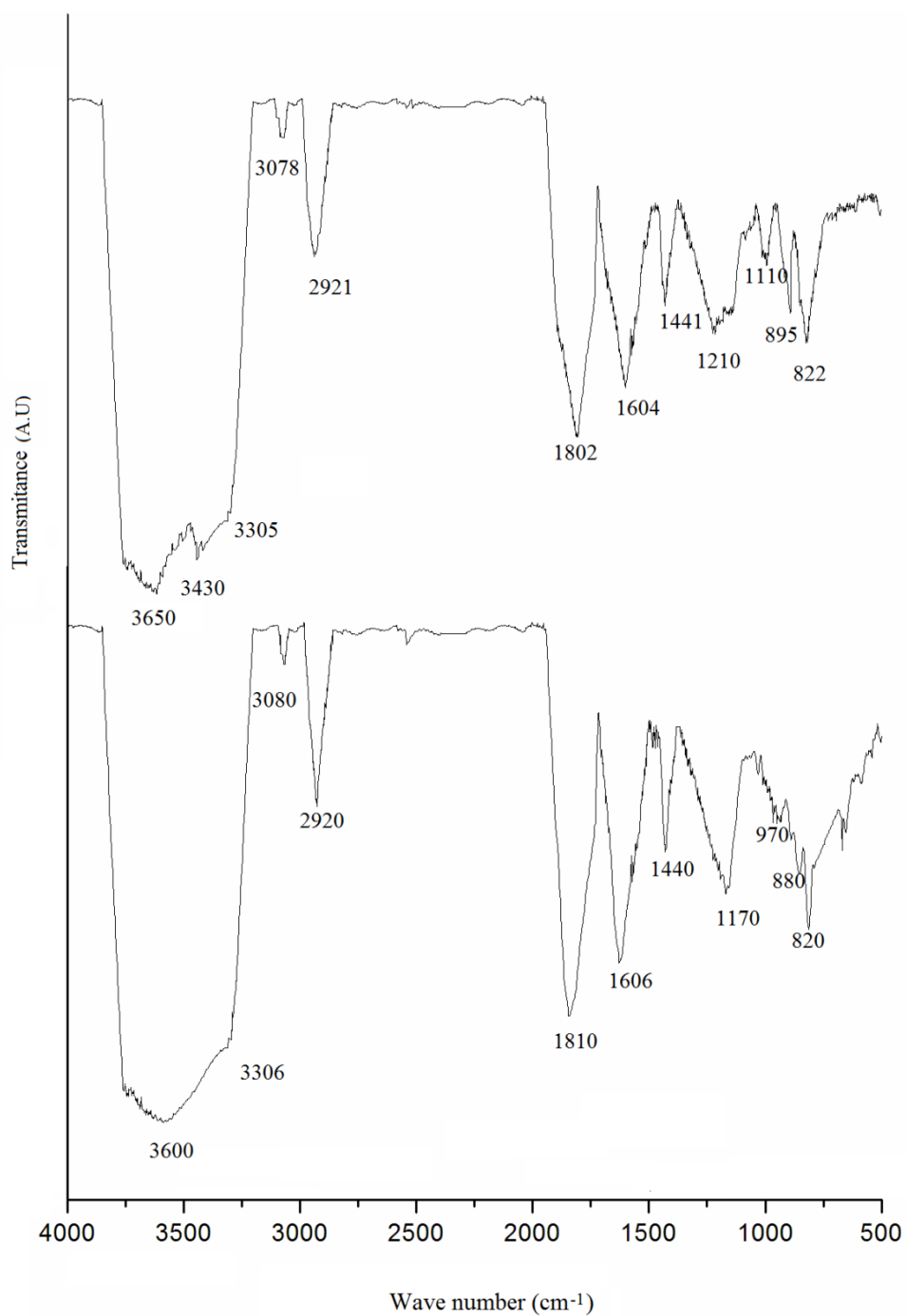


Fig.3.29. FTIR spectra of original antioxidants (a) RHE (b) SDE

**Table: 3.5(a). Major Absorption Peaks Observed and Assigned Configurations in FTIR Spectrum of RHE**

Position (cm ⁻¹)	Intensity	Assigned configuration
880	Medium	CH ₂ (bend) aromatic
970	Weak	C-H (bend) aromatic
1170	Strong	C-O stretching phenolic
1440	Strong	C-H (bend) aliphatic
1606	medium	C = C (stretch) aromatic
1810	Strong	C=O (stretch) carbonyl
2920	Medium	CH ₂ (bend) aliphatic
3080	Strong	CH ₂ (bend) aliphatic/aromatic
3306-3600	Strong	O-H (stretch)Phenolic

Table: 3.5 (b). Major Absorption Peaks Observed and Assigned Configurations in FTIR Spectrum of SDE

Position (cm ⁻¹)	Intensity	Assigned configuration
822	Medium	CH ₂ (bend) aromatic
895	Weak	C-H (bend) aromatic
1210 & 1110	Medium	C-O(stretching) ether,phenolic
1441	Strong	C-H (bend) aromatic
1604	medium	C = C (stretch) aromatic
1802	Strong	C=O (stretch) carbonyl
2921	Medium	CH ₂ (bend) aliphatic
3078	Strong	CH (bend) aliphatic/aromatic
3305-3600	Strong	O-H (Stretch)Phenolic



3.3.1.2. FTIR Analysis of Original Base Oil Before Oxidation

The FTIR data obtained in case of the original base oil (un-oxidized) is provided in Table 3.6 and the respective spectrum is displayed in Fig. 3.30 (a). Well developed absorption peaks can be observed at 2939 and 2850 cm^{-1} corresponded to the CH and CH_2 stretching vibrations. Pronounced bands at 1377 and 1475 cm^{-1} can also be observed corresponded to the CH, CH_3 bending vibrations (deformations). Some medium intensity peaks mostly centered at 721 cm^{-1} are evident indicative of CH_2 bending. Some weak intensity bands centered at 981 and 2788 cm^{-1} can also be observed which evident the CH bending and CH_3 stretching vibrations, respectively. The presence of these peaks indicates the paraffins which are characterized by CH, CH_2 and CH_3 vibrations [37]. The spectrum also exhibits bands appearing at 874 and 1610 cm^{-1} due to CH bending and C=C stretching, respectively which can be corresponded to unsaturated hydrocarbons either aromatic or olefin contents. A well developed band at 1145 cm^{-1} characterizing the C-O stretching vibrations which confirm R-O-Ar functionalities like alkyl aryl ether or aromatic ether can also be observed. A Peak corresponded to aromatics can be observed at 3151 cm^{-1} showing the CH stretching vibrations [39, 42].

It can be observed from the results that the intensities of the peaks corresponded to paraffinic hydrocarbons are high which indicate their presence in high concentration. Conversely, the bands corresponded to aromatic or olefinic hydrocarbons have poor intensities which may be accounted for its low concentration.

Size of the band in a spectrum in case of saturated and unsaturated hydrocarbons or other compounds is a function of concentration of particular group of a compound [8]. The Percent Transmittance (PT) in case of bands characteristic of saturated hydrocarbons indicate their high concentration. The low PT is also indicative of high concentration of a component in the sample.

Thus, it may be inferred from the results that the base oil is comprised mostly of long chain paraffins as the major components and the aromatics as well as olefins as the least concentrated components [37, 42].

**Table: 3.6. Major Absorption Peaks Observed and Assigned Configurations in FT-IR Spectrum of the Original (un-oxidized) Base Oil**

Position(cm^{-1})	Intensity	Assigned configuration
721	Medium	CH_2 (bend) aliphatic
874	Weak	C-H (bend) aliphatic
981	Weak	C-H (bend) aliphatic
1145	Weak	R-O-Ar (St) Alkyl aryl ether or aromatic ether
1201	Medium	C-O(stretching)ether,phenolic
1377	Strong	C-H (bend) aliphatic
1475	Strong	CH_3 (bend) aliphatic
1610	Weak	C = C (stretch) aromatic
2788	Weak	CH_3 (stretch) aliphatic
2850	Strong	CH_2 (bend) aliphatic
2939	Strong	CH (bend) aliphatic
3151	Strong	CH (stretch) aromatic

3.1.1.3. FTIR Analysis of Base Oil Samples after Oxidation at 100 °C for 06 Hours

The FTIR spectra of the un-additized and RHE-&SDE-additized samples oxidized at 100 °C for 06 h are illustrated in the Fig.3.30 (b), Fig.3.30 (c) & Fig.3.30 (d). The corresponding data has been compiled in Table 3.7. Some common bands can be observed in all of the given spectra in the wave number range of 1354, 1477, 2923, 2850 and 721 cm^{-1} which represent the C-H bond vibrations.

No significant changes can be observed for C-H bond in case of the un-additized base oil before and after oxidation performed at 100 °C. However, prominent differences between the original and degraded samples can be observed in case of peaks appearing at 1735 (C=O) and 1600-1610 cm^{-1} (C=C) [43]. It can be observed from the results that in case of the original oil sample (Fig. 3.30 (a)), the peaks in the same wave number range are either absent or invisible which may be due to low concentration of these compounds. While the peaks in the same wave number range are distinct in case of the un-additized



sample after oxidation due to high concentration of carbonyl compounds and olefins as oxidized products [44].

The FTIR spectra of the RHE- and SDE- additized base oil samples after oxidation are accumulated in Fig.3.30 (c) & Fig.3.30 (d), respectively. The FTIR spectrum of the un-additized oil after oxidation at 100 °C is also given for comparison as shown in Fig. 3.30 (b).

The spectra feature various weak, medium and large intensity peaks corresponded to saturated paraffinic hydrocarbons, aromatics/olefins and carbonyl compounds. The distinct large bands observed for saturated hydrocarbons in case of all of the oxidized samples centered at 1377, 1472, 2865 and 2955 cm^{-1} can be seen which can be attributed to CH, CH₃, bending and CH₂, CH stretching vibrations, respectively. Other representative peaks can be seen which can be assigned to saturated hydrocarbons. For instance; one medium intensity peak at 721 cm^{-1} and two weak intensity peaks centered at 965 and 2760 cm^{-1} which may be ascribed to CH₂, CH bending and CH₃ stretching vibrations, respectively. In the wave number range of 1600-1610 cm^{-1} a medium intensity peak and a weak band at 810 cm^{-1} indicate C=C (stretching) and CH (bending) vibrations showing unsaturated hydrocarbons (aromatic or olefinic content). Presence of carbonyl compounds (ester) was confirmed by the appearance of a medium intensity peak at 1735 cm^{-1} . For the oxidized products; ester, a small peak centered at 1156 cm^{-1} can be observed which may be resulted due to C-O stretching vibrations [44].

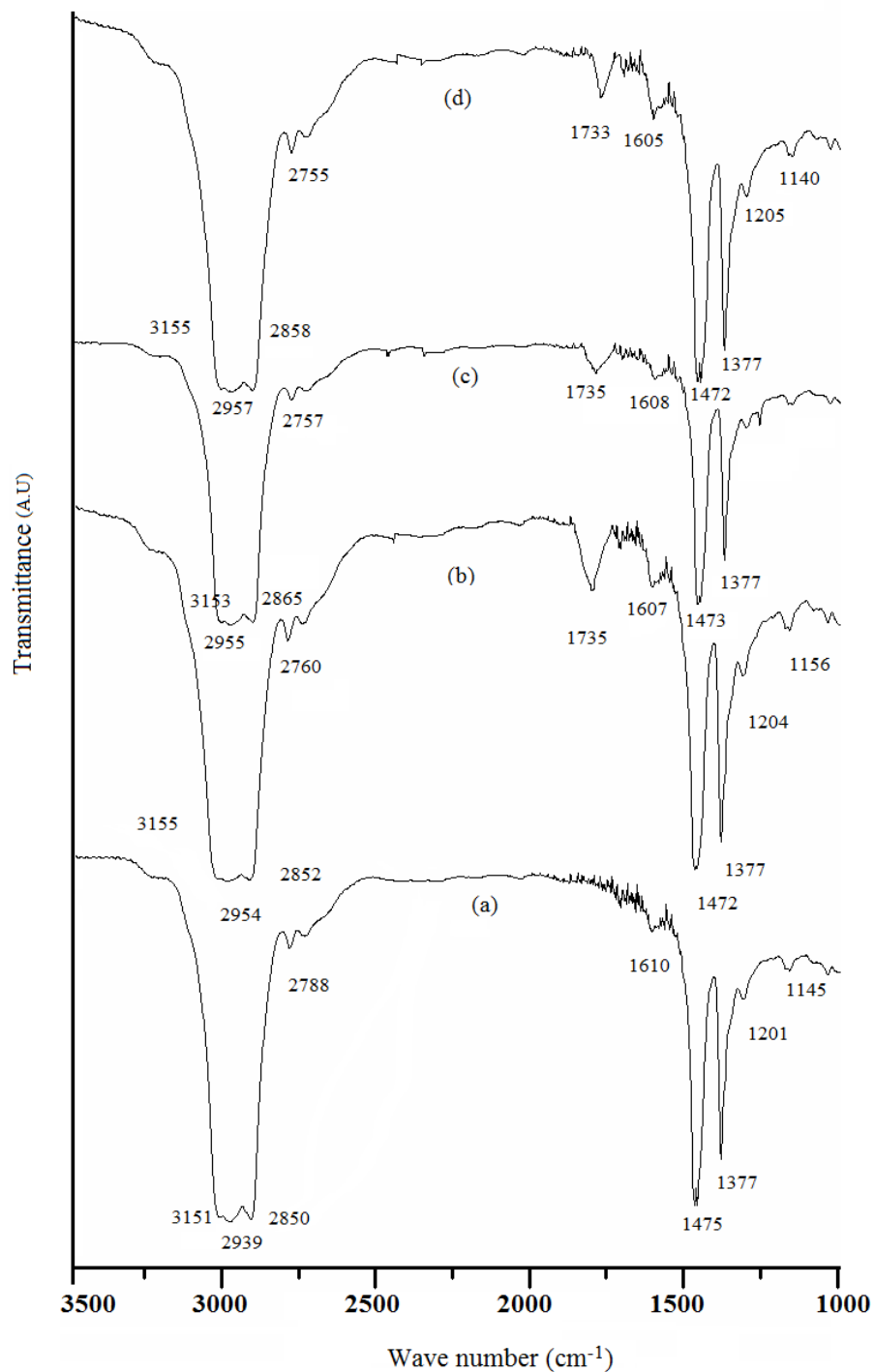


Fig.3.30. FTIR spectra of original and various oxidized samples (a) original base oil (b) un-additized base oil oxidized at 100 °C (c) RHE-additized base oil oxidized at 100 °C and (d) SDE- additized base oil oxidized at 100 °C



As reported elsewhere, the region for the study of oxidation products is 1650-1800 cm^{-1} [45]. The expanded/partial spectra for the original base oil and the un-additized base oil oxidized at 100 °C are given in Fig. 3.31 (a) & Fig. 3.31 (b). The areas under these curves were calculated using computer software. The results are compiled in Table 3.8. According to the data, the non-degraded (original) and degraded (oxidized) samples without antioxidants presented differences in area of spectral bands, for instance carbonyl ($\text{C}=\text{O}$, 1700-1800 cm^{-1}) and aromatic or olefin bands ($\text{C}=\text{C}$, 1500-1670 cm^{-1}) indicating occurrence of oxidation reactions. During thermo-oxidative reactions, products that are harmful to the effective working of the oil may be formed thereby changing its properties [46].

Table: 3.7(a).Major Absorption Peaks Observed and Assigned Configurations in FTIR Spectrum of Un-additized Base Oil Oxidized at 100 °C

Position (cm^{-1})	Intensity	Assigned configuration
721	Medium	CH_2 (bend) aliphatic
810	Weak	C-H (bend) aliphatic
965	Weak	C-H (bend) aliphatic
1156	Weak	R-O-Ar (Str) Alkyl or aryl ether
1204	Medium	C-O(Stretch) Ether, Phenol
1377	Strong	C-H (bend) aliphatic
1472	Strong	CH_3 (bend) aliphatic
1607	Weak	C = C (stretch) aromatic
1735	medium	$\text{C}=\text{O}$ (stretch) ester
2760	Weak	CH_3 (stretch) aliphatic
2852	Strong	CH_2 (bend) aliphatic
2954	Strong	CH (bend) aliphatic
3155	Strong	CH (stretch) aromatic



Table: 3.7(b). Major Absorption Peaks Observed and Assigned Configurations in FT-IR Spectrum of RHE-Additized Base Oil Oxidized at 100 °C

Position (cm ⁻¹)	Intensity	Assigned configuration
721	Medium	CH ₂ (bend) aliphatic
845	Weak	C-H (bend) aliphatic
956	Weak	C-H (bend) aliphatic
1175	Weak	R-O-Ar (St) Alkyl or aryl ether
1377	Strong	C-H (bend) aliphatic
1473	Strong	CH ₃ (bend) aliphatic
1606	Weak	C = C (stretch) aromatic
1735	medium	C=O (stretch) ester
2757	Weak	CH ₃ (stretch) aliphatic
2865	Strong	CH ₂ (bend) aliphatic
2955	Strong	CH (bend) aliphatic
3153	Strong	CH (stretch) aromatic



Table: 3.7(c).Major Absorption Peaks Observed and Assigned Configurations in FTIR Spectrum of SDE-Additized Base Oil Oxidized at 100 °C

Position(cm^{-1})	Intensity	Assigned configuration
721	Medium	CH_2 (bend) aliphatic
825	Weak	C-H (bend) aliphatic
970	Weak	C-H (bend) aliphatic
1140	Weak	R-O-Ar (St) Alkyl or aryl ether
1205	Medium	C-O(Stretch) Ether, Phenol
1377	Strong	C-H (bend) aliphatic
1472	Strong	CH_3 (bend) aliphatic
1605	Weak	C = C (stretch) aromatic
1733	medium	C=O (stretch) ester
2755	Weak	CH_3 (stretch) aliphatic
2858	Strong	CH_2 (bend) aliphatic
2957	Strong	CH (bend) aliphatic
3155	Strong	CH (stretch) aromatic

The expanded/partial FTIR absorbance spectrum of C=O and C=C bands of the original oil before and after oxidation have been shown in Fig. 3.31 (a) and Fig. 3.31 (b). The carbonyl compounds and aromatics are quantified by observing area under the concerned bands in terms of PAI value which possess linear relationship with the level of thermo-oxidative degradation of oil. In case of the original un-oxidized base oil, the PAI values for C=O band ($1735\text{-}1900\text{ cm}^{-1}$) was found to be $28\text{ Abs.cm}^{-1}/\text{mm}$ and for C=C band ($1500\text{-}1670\text{ cm}^{-1}$) was $70\text{ Abs.cm}^{-1}/\text{mm}$. The PAI calculated in case of the original oil after oxidation was found to be $302\text{ Abs.cm}^{-1}/\text{mm}$ for C=O band in spectral region $1735\text{-}1851\text{ cm}^{-1}$ which indicate significant level of degradation as confirmed from the spectrum exhibiting a medium carbonyl band at 1735 cm^{-1} which indicate ester formation as degraded product of paraffin oxidation.

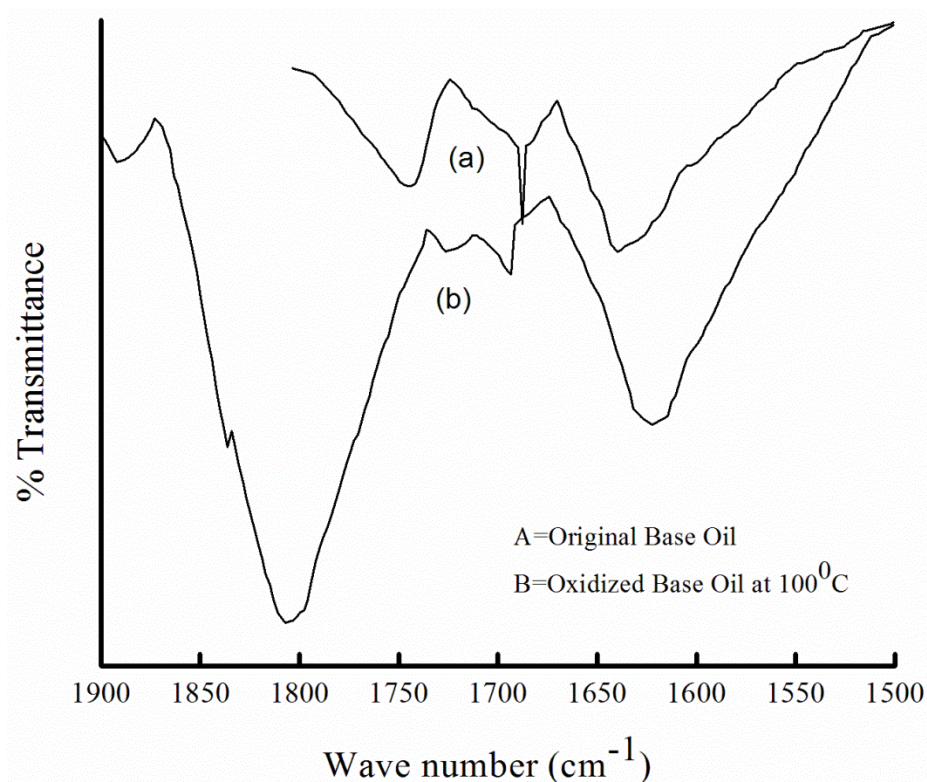


Fig.3.31. Partial FTIR spectra in absorbance mode (Range 1500-1900 cm^{-1}) of base oil samples (a) original base oil before oxidation (b) original base oil after oxidation at 100°C

Similarly, PAI value in case of $\text{C}=\text{C}$ band was found to be $142 \text{ Abs.cm}^{-1} / \text{mm}$ which reveals significant concentration of aromatics in the oxidized sample as confirmed from a medium intensity peak centered at 1504 cm^{-1} due to $\text{C}=\text{C}$ vibrations. Thus, the base oil sample without antioxidants was suffered from oxidation and changes were observed in the spectral region of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ characteristic bonds which indicate its significant degradation.

In the FTIR spectrum, absorbance for a particular spectral band is also an important quantitative indicator for a specific class of compounds in terms of peak height (PH). Increase in intensity of absorbance extends the PH value that in turn shows the increase in concentration of that particular family of compounds as stated by Beer-Lambert law [38]. The PH value determined in case of base oil sample before oxidation for $\text{C}=\text{O}$ band was found to be 0.22 Abs and $\text{C}=\text{C}$ peak, was observed to be 0.15 Abs. In

the same way, PH values for C=O and C=C bands in the aforementioned spectral range were found to be 0.52 and 0.38 Abs in case of base oil after oxidation, respectively.

To investigate the level of degradation, number of times (NOTs) differences in PAI and PH values were calculated between the original base oil sample and the oil samples oxidized at 100⁰C. The difference calculated between the original and the un-additized base oil oxidized at 100⁰C in terms of PAI values for C=O and C=C bands were found to be 9.785 and 1.028 times, respectively. Likewise, the differences in terms of PH values between the original and the base oil samples oxidized at 100⁰C determined for C=O and C=C peaks were found to be 1.363 and 1.533 times. It evidences that percent difference is much larger in case of carbonyl compounds and significant in aromatics/olefin contents between the original and oxidized oil samples. The results are graphically represented in Fig.3.32-Fig.3.33.

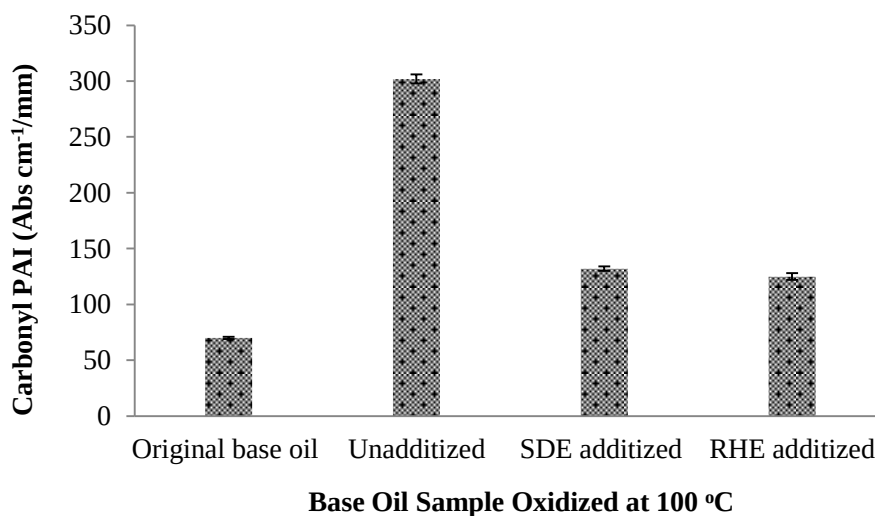


Fig.3.32.Evaluation of PAI (Peak Area Increase) under carbonyl band for original, un-additized, RHE- and SDE- additized base oil samples oxidized at 100 ⁰C. Experimental conditions used: oxidation time: 06 h and antioxidants concentration: 3%

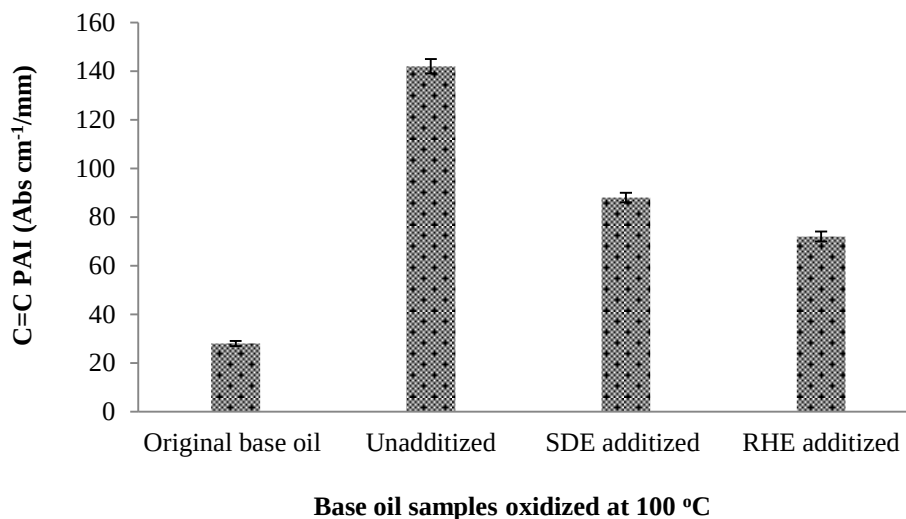


Fig.3.33.Evaluation of PAI (Peak Area Increase) under C=C band for original, un-additized, RHE-and SDE- additizedbase oil samples oxidized at 100 °C. Experimental conditions uaewd: oxidation time: 06 h and antioxidants concentration: 3%

The FTIR partial/ expended spectra of the RHE-and SDE additized base oil samples after oxidation are given in Fig 3.34(a), Fig 3.34 (b) &Fig 3.34 (c) in comparison to the u-additized base oil oxidized under the same set of experimental conditions. The spectra show that both of the antioxidants have markedly reduced the intensity of the spectral bands appearing around 1735 and 1505 cm⁻¹.

The corresponding PAI and PH values were also calculated. The results given in the Fig.3.3.32 &Fig.3.33 indicate a decrease in C=O and C=C bands size which in turn reveal reduction in level of degradation [46, 47].

In case of the RHE-additized base oil sample, the PAI value calculated for C=O band (1735-1851 cm⁻¹) was found to be 125 Abs.cm⁻¹ /mm and for C=C band found to be 72 Abs.cm⁻¹ /mm. While in case of the SDE- additized sample, the PAI value assigned to C=O band (1735-1800 cm⁻¹) was found to be 132 Abs.cm⁻¹ /mm and to C=C band (1604-1649 cm⁻¹) was 81 Abs.cm⁻¹ /mm.

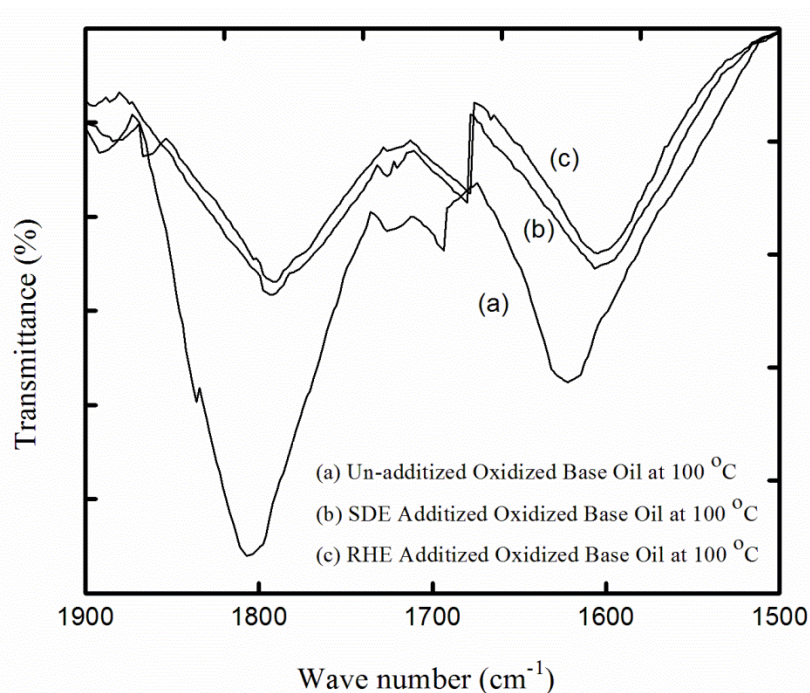


Fig.3.34. Partial FTIR spectra in absorbance mode (Range 1500-1900 cm^{-1}) of various base oil samples oxidized at 100 °C (a) un-additized (b) RHE-additized (c) SDE-additized

The number of times (NOTs) differences between the un-oxidized and RHE-additized base oil samples in terms of CAI values for C=O spectral band was also calculated which were found to be 3.464 times and for C=C band was 0.028 times. In case of the SDE-additized base oil sample, the NOTs differences in comparison with the un-additized base oil (oxidized) determined for C=O and C=C peaks (CAI) were found to be 3.714 and 0.157 times, respectively. Similarly, NOTs of PH values in case of the RHE-additized sample for C=O band noticed was 0.090 times and for C=C peak was 0.533 times in comparison with un-oxidized oil. While for the SDE, the differences for C=O and C=C bands were found to be 0.272 and 0.666 times, respectively.

The PH value possesses linear relation with concentration of compounds containing the same functional group. The PH values for the C=O and C=C peaks within the same spectral range as mentioned (before for CAI) in case of the RHE-additized sample noted to be 0.24 and 0.23 Abs, respectively. For C=O and C=C, peaks belong to

the same spectral range, the PH values observed for the SDE-additized sample were 0.28 and 0.25 Abs, respectively.

Overall, CAI and PH values in case of the un-additized base oil were significant, low for the RHE and SDE-additized samples and minor for the original un-oxidized sample.

It can be concluded that the CAI and PH values determined for both of the C=O and C=C bands followed the order as:

Non-additized > SDE-additized > RHE-additized > original base oil

This order signifies that the concentration of carbonyl compounds and aromatic or olefin contents of the oxidized base oil samples found mostly in case of the un-additized samples, more in the SDE-additized and least in the RHE-additized sample while minor in the original base oil sample as presented in Fig. 3.35 and Fig.3.36.

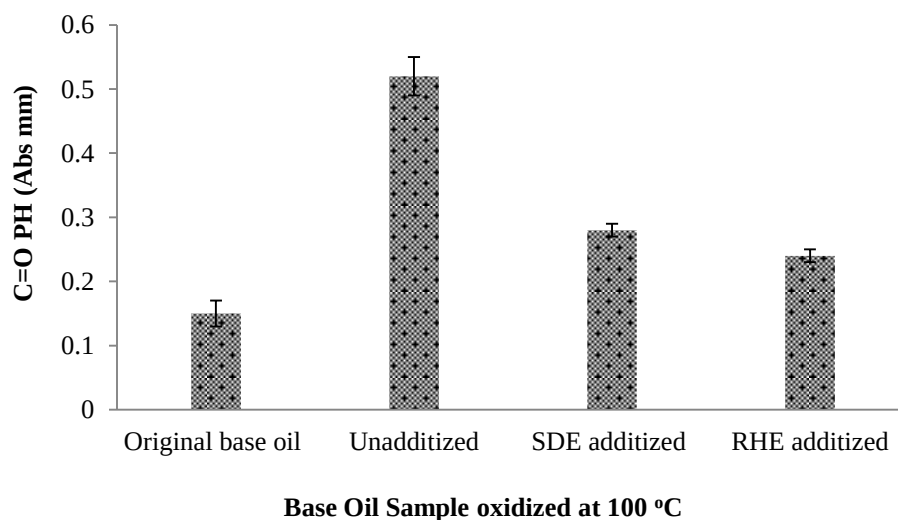


Fig-3.35. Evaluation of PH (Peak Height) under C=O band for original, un-additized, RHE- and SDE-additized base oil samples oxidized at 100 °C. Experimental conditions used: oxidation time: 06 h and antioxidants concentration 3%

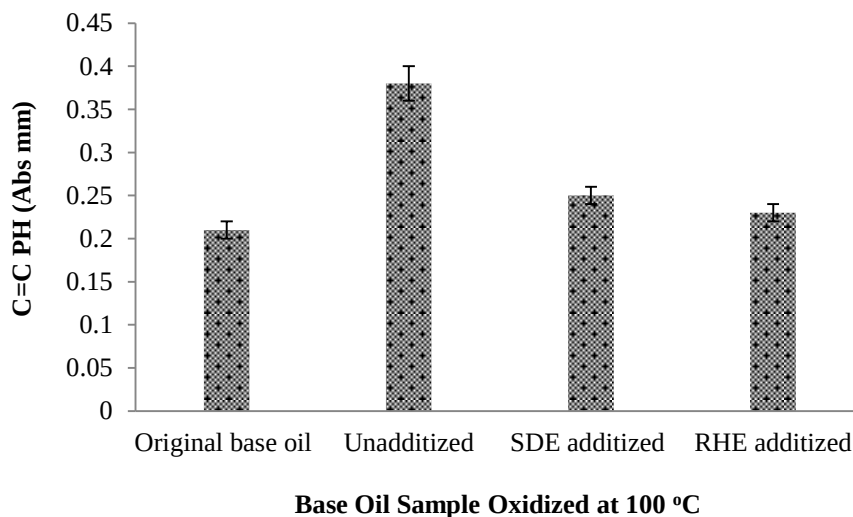


Fig.3.36.Evaluation of PH (Peak Height) under C=C band for original, un-additized, RHE- and SDE-additized base oil samples oxidized at 100 °C. Experimental conditions used: oxidation time: 06 h and antioxidants concentration: 03%

The results indicate that the use of antioxidants reduced the level of degradation to larger extent as clear from the NOTs difference of additized oil and un-additized samples in terms of CAI and PH values. Thus, RHE-additized sample inhibited the level of degradation in comparison with un-additized oil in terms of C=O and C=C peaks reduction to 6.321 and 1.00 times (CAI % reduction) and in terms of NOTs reduction in PH values to 1.273 and 1.00 times by decreasing the concentration of carbonyl and aromatic/olefin contents, respectively. Likewise, the SDE too declined the thermo-oxidative degradation degree in terms of C=O and C=C peaks reduction to 5.991 and 0.871 times (CAI NOTs reduction) and to 1.091 and 0.867 times (PH NOTs reduction), respectively.

In this way, the three oxidized base oil samples and the original one followed the order in terms of CAI and PH values and size of C=O and C=C bands as:

Un-additized > SDE-additized > RHE-additized > original base oil



3.1.1.4. FTIR Analysis of Base Oil Samples After Oxidation at 200 °C for 06 Hours

The FTIR analyses of the base oil samples oxidized at 200 °C for time duration of 06 h were also performed. Similar behavior (as exhibited at 100°C) was shown by the base oil samples when oxidized at 200°C except for the size of C=O and C=C peaks as shown in Fig. 3.37 (a), Fig. 3.37 (b), Fig. 3.37 (c) & Fig. 3.37 (d) and Table 3.8. The results indicate that all of the oxidized base oil samples consisted of similar various spectral bands for C-H bond vibrations including some large intensity peaks (1377, 1451, 2850 and 2952 cm^{-1}), medium intensity peaks (721 and 961 cm^{-1}), and a poor intensity appearing at 2750 cm^{-1} . A medium band centered at 1505-1615 cm^{-1} and a weak at 810 cm^{-1} present C=C (stretching) and CH (bending) vibrations which indicate the presence of aromatic or olefins in the samples under study. Some peaks correspond to ester as product of oxidation can be observed at 1732 cm^{-1} which presents the C=O stretching vibrations and at 1160 cm^{-1} which may be resulted due to C-O stretching vibrations [37].

Fig.3.38 & Fig. 3.39 display the FTIR region of interest of the various oxidized samples in comparison with the original oil in expended form. The results indicate that the area under spectral band positioned at 1735 (C=O) and 1600 (C=C) get wider and deeper with increase in temperature from 100 to 200 °C indicating significant degradation.

Increase in size of the band for ester (C=O) and aromatic/olefin (C=C) in case of the oxidized sample in comparison to the original un-oxidized sample indicates the increase in the degree of the degradation. Fig.3.38 also verified the fact that level of the degradation is a function of temperature as size of C=O and C=C spectral bands at 200°C is larger than at 100°C. Size of the C=O and C=C bands is a function of concentration of the carbonyl and aromatic degraded products.

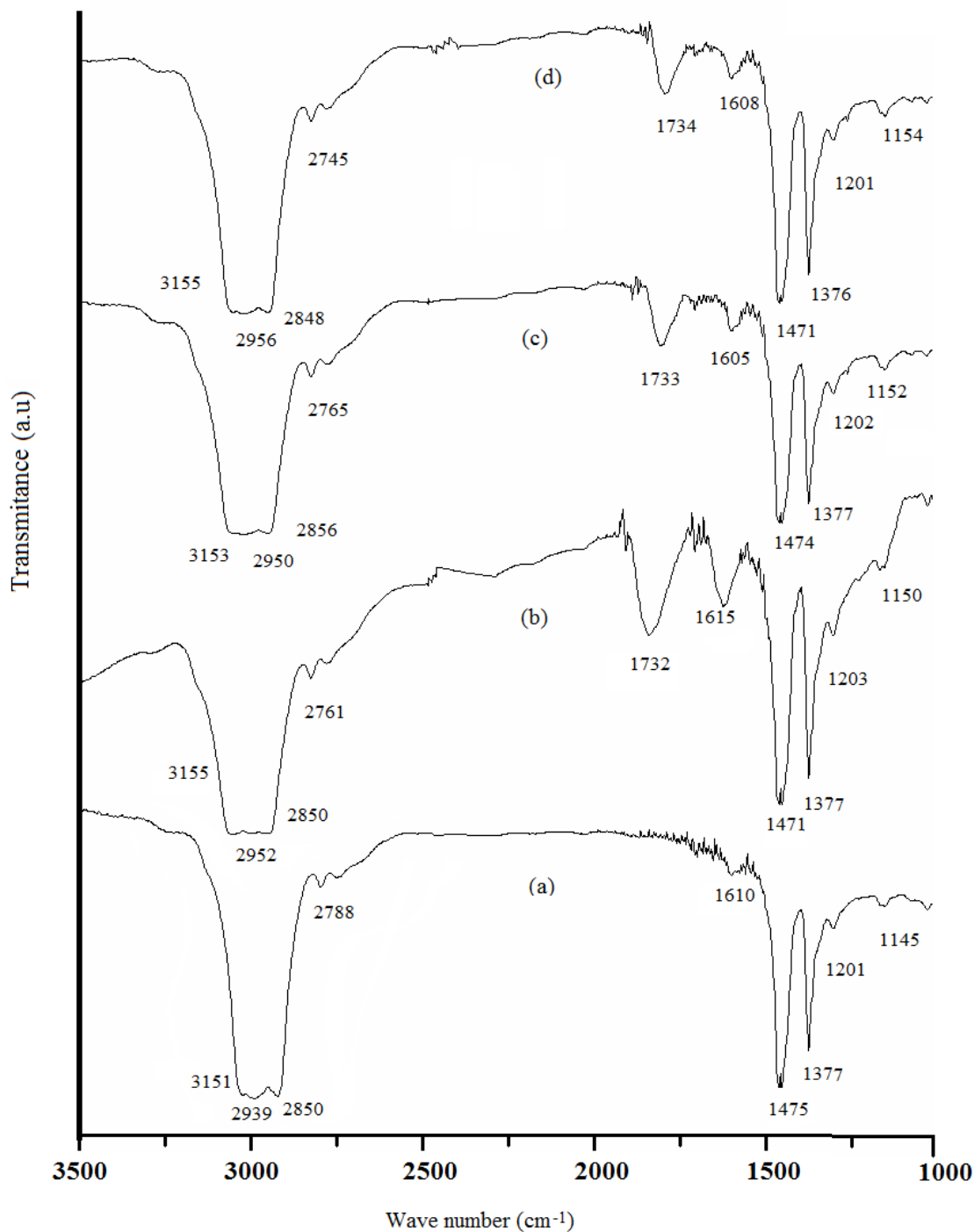


Fig.3.37. FTIR spectra of original and various oxidized samples (a) original base oil (b) un-additized base oil oxidized at 200 °C (c) RHE-additized base oil oxidized at 200 °C and (d) SDE-additized base oil oxidized at 200°C



Table: 3.8(a). Major Absorption Peaks Observed and Assigned Configurations in FTIR Spectrum of Un-additized Base Oil Oxidized at 200 °C

Position(cm^{-1})	Intensity	Assigned configuration
721	Medium	CH_2 (bend) aliphatic
811	Weak	C-H (bend) aliphatic
961	Weak	C-H (bend) aliphatic
1150	Weak	R-O-Ar (St) Alkyl aryl ether or aromatic ether
1203	Medium	C-O (Str) Ether
1377	Strong	C-H (bend) aliphatic
1471	Strong	CH_3 (bend) aliphatic
1615	Weak	C = C (stretch) aromatic
1732	medium	C=O (stretch) ester
2761	Weak	CH_3 (stretch) aliphatic
2850	Strong	CH_2 (bend) aliphatic
2952	Strong	CH (bend) aliphatic
3155	strong	CH (Stretch) aromatic

**Table: 3.8(b).Major Absorption Peaks Observed and Assigned Configurations in FTIR Spectrum of RHE-Additized Base Oil Oxidized at 200 °C**

Position (cm ⁻¹)	Intensity	Assigned configuration
721	Medium	CH ₂ (bend) aliphatic
840	Weak	C-H (bend) aliphatic
953	Weak	C-H (bend) aliphatic
1152	Weak	R-O-Ar (St) Alkyl aryl ether or aromatic ether
1202	Medium	C-O (Str) Ether
1377	Strong	C-H (bend) aliphatic
1474	Strong	CH ₃ (bend) aliphatic
1605	Weak	C = C (stretch) aromatic
1733	medium	C=O (stretch) ester
2765	Weak	CH ₃ (stretch) aliphatic
2856	Strong	CH ₂ (bend) aliphatic
2950	Strong	CH (bend) aliphatic
3153	Strong	CH (stretch) aromatic



Table: 3.8(c).Major Absorption Peaks Observed and Assigned Configurations in FTIR Spectrum of SDE-Additized Base Oil Oxidized at 200 °C

Position (cm ⁻¹)	Intensity	Assigned configuration
721	Medium	CH ₂ (bend) aliphatic
835	Weak	C-H (bend) aliphatic
968	Weak	C-H (bend) aliphatic
1154	Weak	R-O-Ar (St) Alkyl aryl ether or aromatic ether
1201	Medium	C-O (Str) Ether
1376	Strong	C-H (bend) aliphatic
1471	Strong	CH ₃ (bend) aliphatic
1608	Weak	C = C (stretch) aromatic
1734	medium	C=O (stretch) ester
2745	Weak	CH ₃ (stretch) aliphatic
2848	Strong	CH ₂ (bend) aliphatic
2956	Strong	CH (bend) aliphatic
3155	Strong	CH (stretch) aromatic

Quantitative increase in level of the degradation with the increase in temperature and an extent, to which these biomass derived antioxidants (RHE and SDE) have reduced the degree of oxidation, was also evaluated in terms of PAI and PH changes as determined in case of oxidation of these samples performed at 100 °C. The PAI values calculated in case of the un-additized base oil oxidized at 200°C for C=O band was found to be 755 Abs.cm⁻¹ /mm and for C=C was 248 Abs.cm⁻¹ /mm as displayed in Fig-3.40 and Fig-3.41. Thus, it possessed the percent difference of about 150 % or (1.50 times) in case of C=O band compared with the same sample when oxidized at 100°C. The NOTs difference between un-additized and original BO samples calculated was 25.964 times.

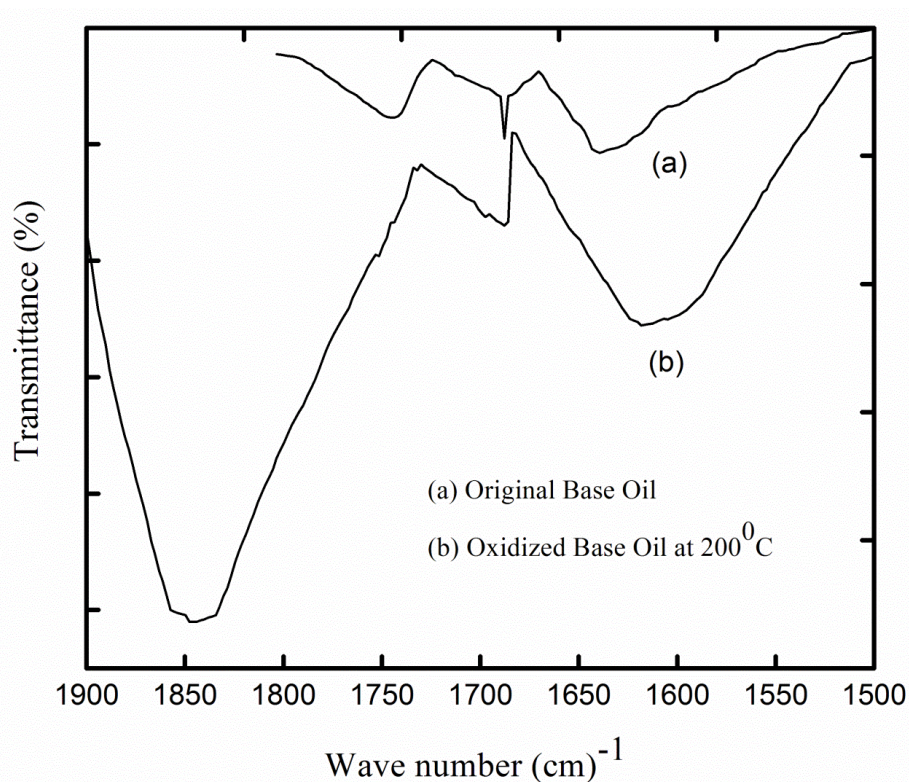


Fig. 3.38. Partial FTIR spectra in absorbance mode (Range 1500-1900 cm⁻¹) of base oil samples (a) original base oil before oxidation (b) original base oil after oxidation performed at 200°C

The results signify the one and a half time increase in level of degradation occurred when the temperature was increased from 100 to 200°C. Similarly, PAI value of C=O band in case of the RHE-additized sample was found to be 300 Abs.cm⁻¹/mm and in case of the SDE-additized sample was 330 Abs.cm⁻¹/mm (Fig. 3.41 & Fig. 3.42). In case of the RHE-additized sample, the NOTs difference determined in PAI value in comparison with the control sample was found to be 9.710 times and in case of SDE-additized sample was 10.785 times. The results indicate the outstanding antioxidant behavior of both antioxidants in terms of avoiding thermo-oxidative degradation of the base oil at 200 °C.

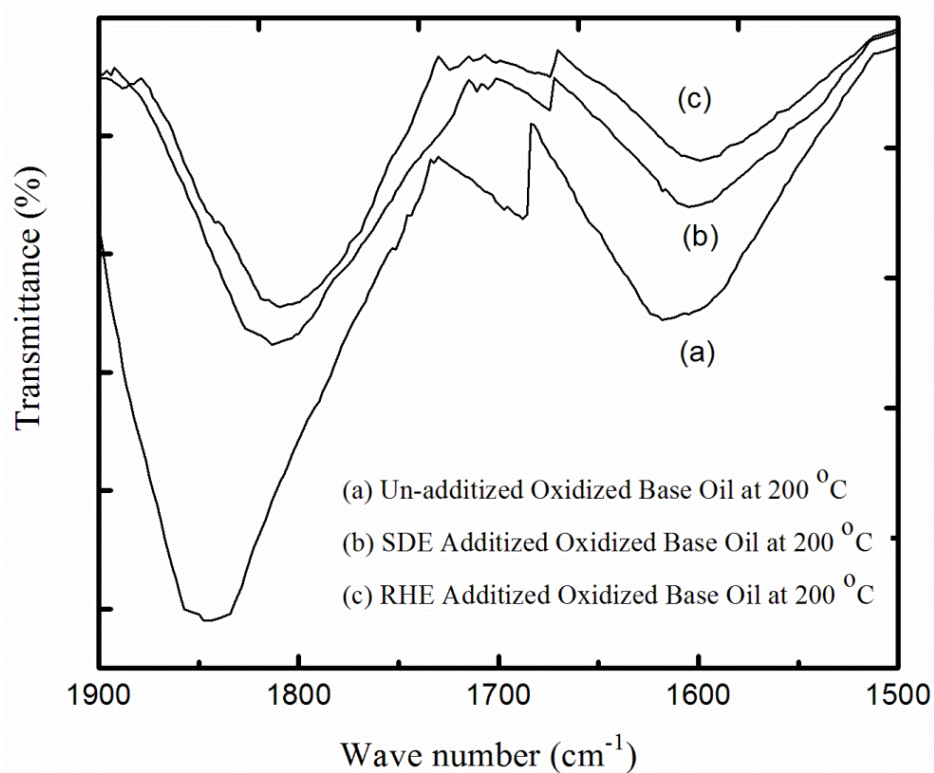


Fig.3.39. Partial FTIR spectra in absorbance mode (Range 1500-1900 cm^{-1}) of base oil samples after oxidation performed at 200 °C (a) original (b) SDE-additized (c) RHE-additized

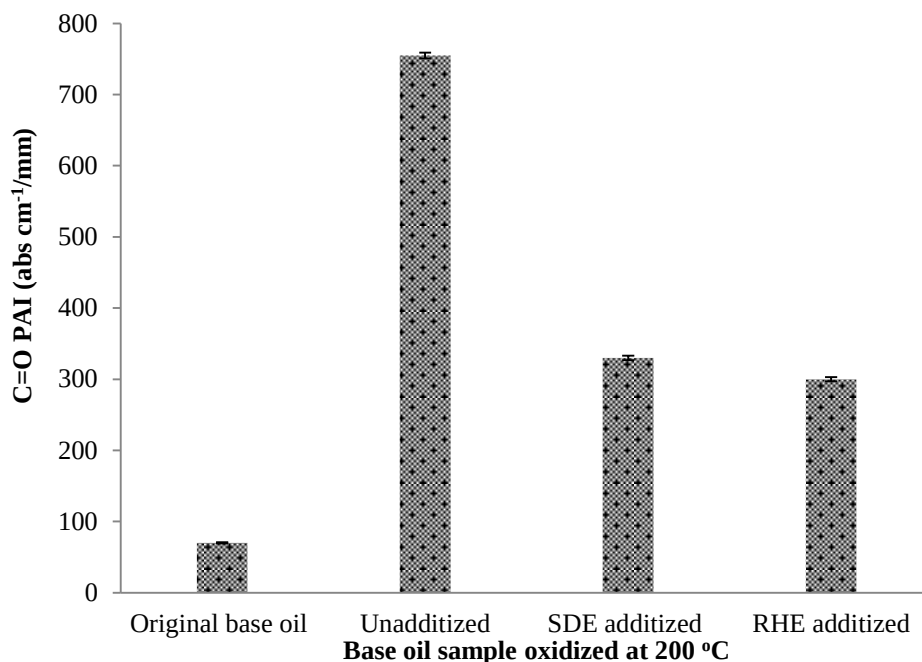


Fig.3.40.Evaluation of PAI (Peak Area Increase) under carbonyl band for the original, un-additized,RHE- and SDE-additized base oil samples oxidized at 200 °C. Experimental conditions used: oxidation time: 06 h and antioxidants concentration: 3%

In the same way, PAI values for C=C band of all the three oxidized samples were determined and compared. The PAI values determined in case of the un-additized base oil for C=C spectral band found was found to be 248 Abs.cm⁻¹ /mm and in case of RHE- and SDE-additized MBO samples were found to be 100 and 128 Abs.cm⁻¹ /mm, respectively. While in case of the base oil oxidized at 100 °C, the value for the same C=C band was found to be 142 Abs.cm⁻¹ /mm. The results indicate that these samples (at 100 and 200°C) possessed 74.64 % difference. NOTs difference determined for PAI C=C band vlaues between un-additized oxidized oil and original oil was 2.542 times. Use of the RHE reduced this NOTs difference to 0.428 times and the SDE to 0.828 times which indicate their excellent antioxidant character. Thus, RHE prevented the level of degradation in terms of reduction in PAI value for C=O band to 16.254 times and for C=C band to 2.114 times. While SDE caused reduction in PAI value for C=O band to

15.179 times and for C=C band to 1.714 times. Thus, the base oil samples followed the order in terms of PAI values for C=O and C=C spectral bands as:

Un-additized>SDE-additized>RHE-additized >original oil

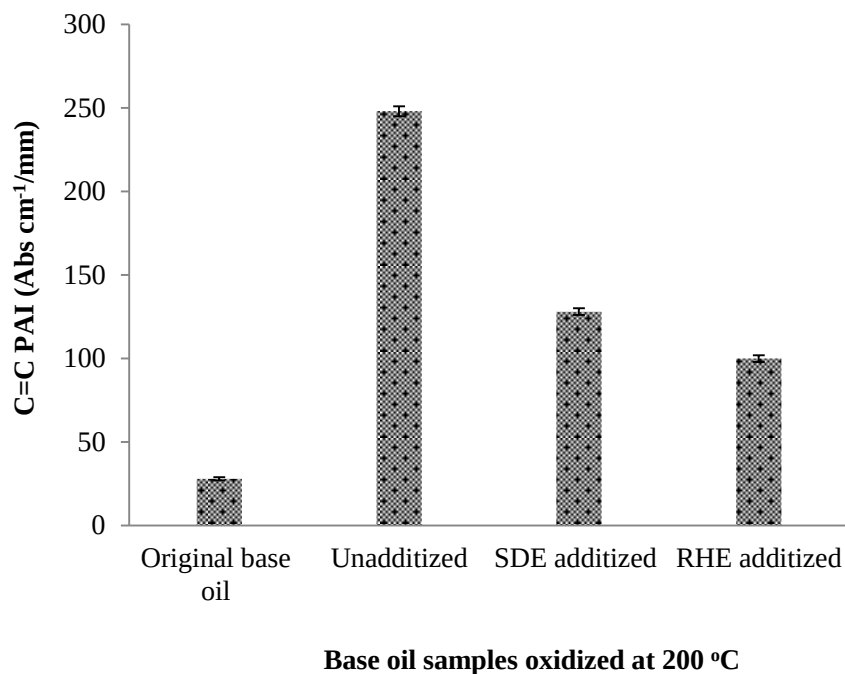


Fig.3.41.Evaluation of PAI (Peak Area Increase) under C=C band for original, un-additized, RHE- and SDE-additizedbase oil samples oxidized at at 200 °C. Experimental conditions used: oxidation time: 06 h and antioxidants concentration: 3%

Beside the PAI parameter, the PH values were also employed for determining the degree of degradation based on intensity of absorbed IR radiations following the Beer-Lambert law. More absorbance in spectral regions of C=O and C=C bands show high concentration of carbonyl and aromatic compounds which indicate higher level of degradation. Therefore, PH values are used as function of degree of degradation which is directly related with oxidation time and temperature. The PH value observed for C=O band in case of the un-additized base oil sample was found to be 1.11 Abs, in case of the RHE- additized sample was found to be 0.45 Abs & in case of SDE-additizedwas 0.55 Abs as shown in Fig-3.42 &Fig-3.43.

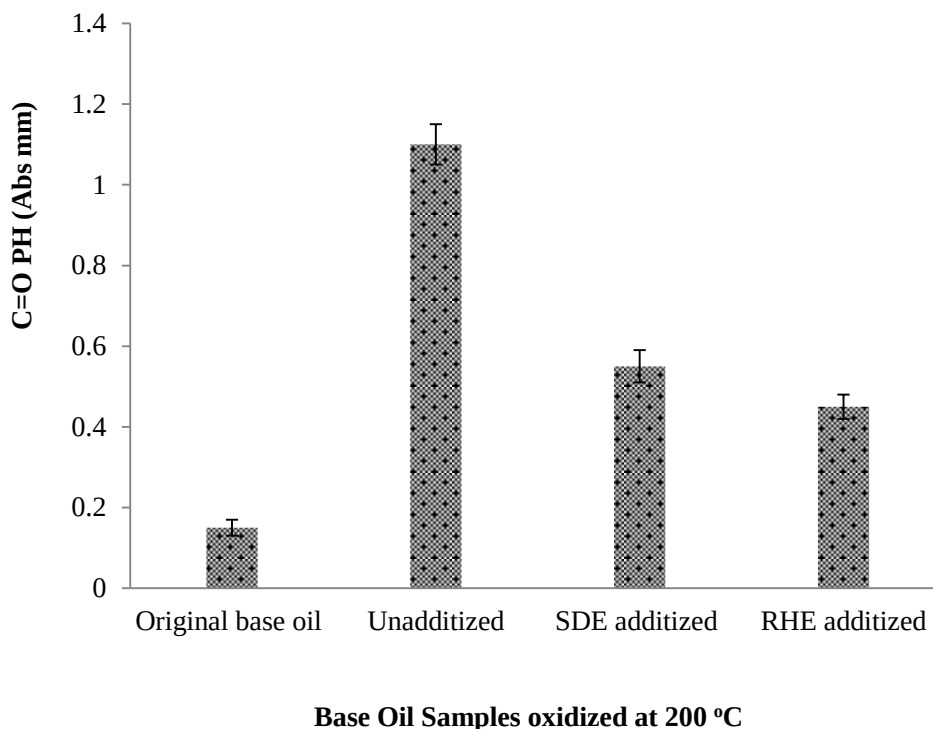


Fig.3.42.Evaluation of PH (Peak Height) under C=O band for original, un-additized, RHE-and SDE-additizedbase oil samples oxidized at 200 °C. Experimental conditions used: oxidation time: 06 h and antioxidants concentration: 3%

NOTs difference in PH values for C=O band between the un-additized sample oxidized at 100°C and 200°C was found to be 1.115 times (111.53 %) and with the original un-oxidized oil was 4.04 times (400%). It indicated a greater level of degradation when temperature was extended from 100 to 200 °C. The NOTs difference calculated in case of RHE-additized was found to be 1.045 times and in SDE-additized case was 1.500 times in comparison with original MBO. The results evidenced that RHE and SDE avoided the degradation to a significant extent. Because the NOTs difference found in case of RHE-additized sample was 2.995 times and in case of SDE-additized sample was 2.540 times in comparison with un-additized oxidized base oil.

Following the same parameter of PH values, changes in terms of C=C spectral band for the three oxidized samples were analyzed. The PH values determined in case of the un-additized, RHE- and SDE-additized oxidized samples were found to be 0.51, 0.24

and 0.32 Abs, respectively as displayed in Fig-3.43. Percent difference determined for C=C band between un-additized sample at 100°C and 200°C was found to be 34.21 % and with the original oil was 2.400 times. This wide difference was reduced with the use of antioxidant and was found to be 0.600 times in case of the RHE and 1.133 times in case of the SDE-additized samples. Thus, RHE inhibited the extent of degradation in terms of reduction in PH value for C=O band to 2.995 times and C=C band to 1.800 times in comparison with un-additized MBO oxidized at 200 °C. While the SDE, caused reduction in terms of PAI value for C=O band to 2.540 time and for C=C band to 1.267 times. Thus, the base oil samples followed the same order as determined for PAI values in terms of PH values for C=O and C= C spectral bands:

Un-additized > SDE-additized > RHE-additized > original oil

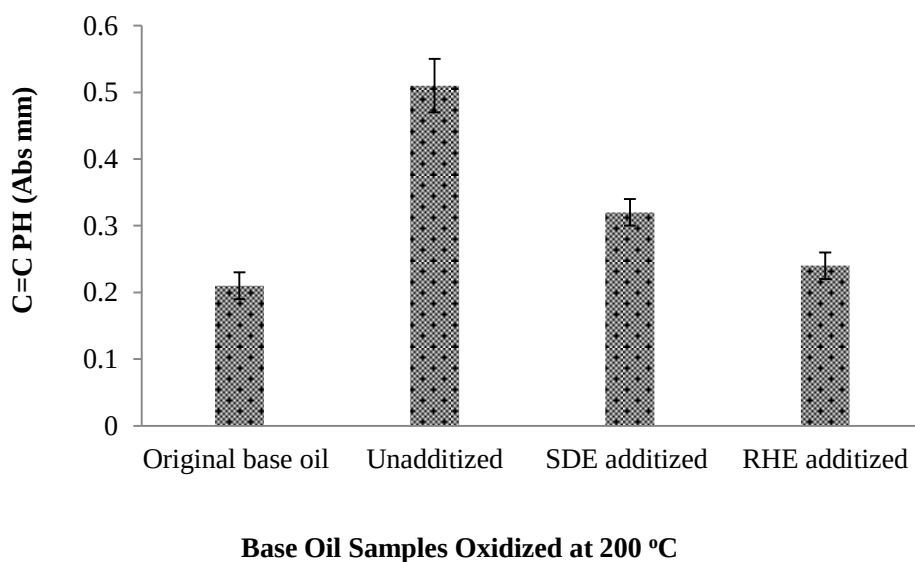


Fig-3.43. Evaluation of PH (Peak Height) under C=C band for original, un-additized, RHE-and SDE- additized base oil samples oxidized at 200 °C. Experimental conditions used: oxidation time: 06 h and antioxidants concentration: 03%)

It can be inferred from the results of the samples oxidized at 100 and 200°C that the abundant ingredients found to be saturated hydrocarbons. Carbonyl compounds and aromatics or olefins were found in least concentrations. The abundant component i.e.



paraffins found to have undergone oxidation leading to a decrease in its concentration with the rise in temperature of oxidation. Moreover, the concentration of the aromatics and carbonyl compounds also increased with the increase in temperature [36]. The un-additized base oil sample was found to be the most degraded due to increase in the size of C=O and C=C bands which further indicated high CAI and PH values. While in case of the RHE-and SDE-additized samples, the CAI and PH values are much lower as compared with the un-additized sample. The results reveal the least level of degradation in case of both of the additized samples. Among the two antioxidants used, RHE found to be the most effective in terms of peak sizes and lowest CAI and PH values. Thus, performance evaluation of RHE and SDE can be viewed as outstanding in preventing quality declination of the base oil at optimum conditions. Furthermore, RHE was found to be more useful in reducing thermo-oxidative degradation to 16.254 times and SDE to 15.179 times for PAI C=O band due to ester as main degraded product when compared with the un-additized base oil having total NOTs difference of 25.964 times under the same set of experimental conditions. Thus, these base oil samples can be ranked in terms of thermo-oxidative stability as:

Original>RHE-additized >SDE-additized> un-additized



PHASE-IV

In this set of experiments, the conductance changes occurring in the oil samples during oxidation were recorded in order to decide about the oxidation induction times (OIT) and oxidative stability index (OSI) which are related to the thermo-oxidative stability of base lubricating oil. The changes were measured for un-additized and RHE- & SDE-additized base oil samples oxidized at 100 and 200 °C for 06 h. The results are presented as under:

3.4. OXIDATIVE STABILITY INDEX (OSI) STUDY

OSI is a physical method used for evaluating the oxidative stability of oil, fats or their derivative like biodiesel samples. It involves the oxidation of oil which evolves the volatile organic acids that are collected in de-ionized water containing conductivity probe to show conductivity rise. At the initial stage of oxidation, peroxides and hydroperoxides are formed as primary products and after some time, the higher hydrocarbons get completely destroyed and the secondary oxidation products formed which include low-molecular organic acids in addition to other volatile organic compounds. The amount of these secondary degraded products is the function of oxidation time and temperature rise. The time period from the start of the OSI oxidation test to the point where no rapid change in conductance is appeared is called induction period/time. It shows that OSI time get started just at the end of induction period. The OSI time may be defined as the moment after induction period where a sudden change in conductance is observed at a particular time during course of oxidation. After induction period, a rapid rise in conductance is observed due to increased rate of oxidation which shows the onset of OSI Time. The induction period shows the oxidative stability of oil. Therefore, induction period is found to be a function of the oxidative stability of oil. Larger is the induction period, high will be the stability of the oil and vice versa. Induction period and OSI time possess direct relation with each other which reveals that oil with larger induction period will have longer OSI time and thus will be highly stable. While the OSI time indicates that resistance to oxidation is overcome. OSI test proceeds slowly at first during induction period because small amount of acid is released and then a sudden change is observed [48].



OSI induction period and time can be illustrated graphically with a plot between conductance and time which is known as oxidograph. It is concerned with OSI time both at low and high temperature oxidation maintained at isothermal conditions. The time period from the start of oxidograph to the point where no rapid change in conductance is appeared is called induction period. While the point in oxidograph where abrupt change in conductance is seen called inflection point or OSI time. OSI is an improved method of AOCS (American Oil Chemists Society) for assessing resistance to oxidation. OSI is more reliable than AOM method (Active oxygen method) because AOM has OSI time <03h and have low precision for high stability oil. OSI measurement is related to Rancimat method because these employed to stability determination of oil. OSI method proceeds slowly at first because during induction period little amount of volatiles are produced [51].

Conductance measurements are observed after each 10 minutes normally and when OSI time is reached then after each 01 minute. These measurements are recorded from a digital conductivity meter. The anti-oxidant effect is evaluated using oil stability index and oxidation which determines the service life of a lubricant. The rate of oxidation or level of degradation can be reduced in the presence of anti-oxidants either natural or additives [49]. The effectiveness or efficiency of antioxidants of all of the natural plants extracts in its blend form with oil can be expressed in terms of stabilization factor (SF) which is given as under:

$$SF = \text{Induction period with Inhibitor} / \text{Induction period without Inhibitor} \times 100.$$

Whereas induction time is taken in hour obtained from Rancimat method [50].

The same parameters were determined for the base oil samples under test in the absence and the presence of the antioxidants under investigation. The results are provided and discussed in the proceeding section.



3.4.1. Oxidative Stability Index of the Original and Various Oxidized Base Oil Samples (Un-Additized, RHE-& SDE Additized)

3.4.1.1. Original (un-oxidized) Base Oil Sample

Conductance measurements were made and OSI time was determined from the curve of rapid change from oxidograph in case of the original base oil. The normal conductance changes were noticed after each 10 min. The data after each 05 hours was tabulated because of significant difference. While the plot of conductance vs. time (oxidograph) has been presented in Fig.3.44. The OSI time was noted as abrupt change in the conductance.

Normal conductance change against the time was recorded in case of the original base oil sample for oxidation time ranges from 05- 40 h with a time interval of 05 h. But after 40 h, a rapid increase can be seen in the conductance which shows the accelerated oxidative degradation rate. Thus, 40 h was found to be the OSI time at 25°C for the original un-oxidized sample as clear from the sharp line in the curve provided in Fig 3.44 [52]. After OSI time, an abnormal conductance was observed when the time was extended from 41 to 90 h with interval of 01 h. Before OSI time, the average per hour change in conductance was found to be 0.030 ms, while after OSI time, was found to be 0.130 ms.

The results revealed that the rate of degradation before the OSI time was insignificant because change in conductance values per h calculated was found to be less than 05 %. After OSI time (40 h), degradation rate become significant due conductance change of above the significant level.

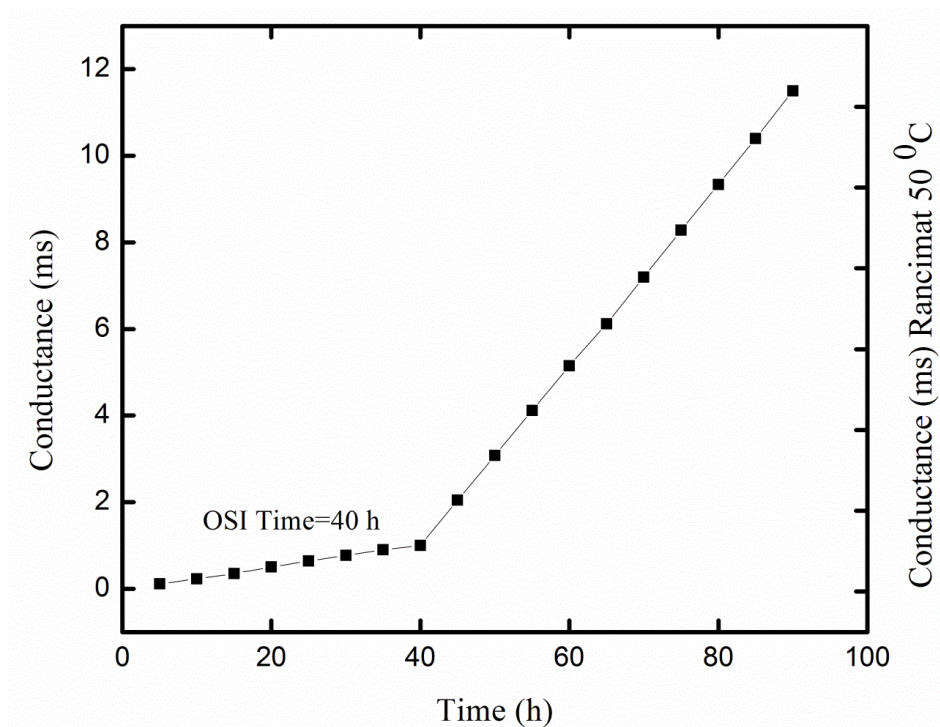


Fig-3.44. Oxidative stability index measurements for un-oxidized (original) base oil

3.4.1.2. OSI Analysis of Various Base Oil Samples Oxidized at 100 °C for 06 Hours

Conductance measurements of the un-additized, the RHE-& SDE –additized samples after oxidation at 100 °C for time duration of 06 h were made and the OSI time was determined from the curve where a rapid change can be observed in oxidograph given in Fig-3.45. The normal conductance changes were noticed whenever a change was occurred (after each 10 min) but tabulated after each 02 h before OSI time and then after each 0.33 h (20 min) after OSI time because of the significant difference in conductance values as per procedure reported elsewhere[53].

The conductance observed in case of the un-additized base oil sample oxidized at 100 °C was found to be normal in the period ranged from 1-36 h as evidenced from the normal straight line. At the start of 37th h, conductance rise was found to be increased many times than the normal change which indicates the arrival of the OSI time. The data of time and conductance revealed that 37h is the OSI time as clear from the sharp erect line provided in Fig-3.45. After OSI time, the conductance recorded after 01 h for the period between 37-80 h. The average per hour difference in conductance during induction

period was 0.040 ms and found to be insignificant and after OSI time was 0.15 ms which indicates a significant change.

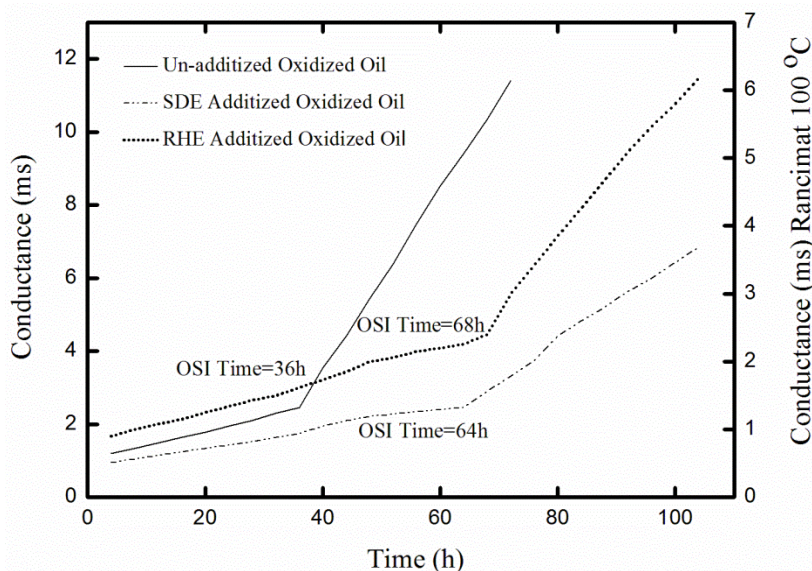


Fig-3.45. Oxidative stability index measurements for un-additized, RHE- and SDE-additized base oil samples oxidized at 100°C

In case of the additized base oil samples, the conductance changes obtained with normal values for time period of 68h in case of RHE-additized sample and were till 64th h in case of SDE-additized sample as clear from the linear lines in Fig-3.45. Thus, induction period determined in case of un-additized base oil was 36h, RHE-additized was found to be 68h and in case of SDE-additized sample was 64h. After 64th and 68th h, a sudden increase in conductance can be seen in case of both of the SDE and the RHE-additized samples as indicated by the sharp lines. Thus, OSI time obtained in case of the un-additized base oil was found to be 36h which was extended to 68h with the use of RHE and to 64h with SDE as antioxidants. It can be observed that antioxidants enhanced the OSI time which may be due to generation of acidic oxidation products [54]. After OSI time, the conductance rise noted in case of RHE and SDE till 100h. The average per hour difference in conductance values determined in case of the RHE-additized sample in induction period was 0.023 ms and after OSI time was 0.045 ms. Similarly, in case of the SDE-additized base oil sample, the average per hour difference in conductance obtained was found to be 0.030 ms before OSI time and after OSI time was found to be 0.048 ms.



The results indicate that before and after OSI time, changes in conductance were found to be insignificant in case of both of the RHE-and SDE-additized samples. Interestingly, RHE as well as SDE converted the significant conductance change after OSI time to insignificant value thus exhibited their novelty as antioxidants.

It can be inferred from the OSI data that the level of degradation was found to be significant at 100⁰C. For un-additized base oil, the OSI time appeared to be 36h which enhanced to 69h in case of RHE-additized and to 65h in case of SDE-additized samples. The results reflect their outstanding antioxidant behavior in base oil samples oxidized at at 100⁰C as per data presented in Fig.3.47. Actually, the abnormal change in conductance was converted to normal that give rise to extension in OSI time in case of both of the RHE-and SDE-additized samples. This increase in OSI time in the presence of the antioxidants is because of conversion of significant change into insignificant before and even after OSI time.

The SF values which can monitor the antioxidant potentials of RHE and SDE were found to be 188.89 and 177.78, respectively as depicted in Fig-3.48. It is thus verified that percent difference in comparison with the oxidized base oil in terms of OSI time achieved in case of the RHE-additized sample was 88.89% and in case of the SDE was 77.78 % as shown in Fig-3.49. The results indicates that RHE extended the service life of base oil to 88.89 % and SDEto 77.78 % in comparison with the un-additized sample. From the values of SF, one can evaluate the outstanding antioxidant behavior of RHE and excellent of SDE. Reproducibility of results and correlation of oxidative evaluation methods can be expressed from the comparison of percent increase in service life and percent change in physico-chemical parameters. Percent increase in useful service life found in case of the RHE was 91.67 % and percent difference for KV appeared was found to be >80 % when compared with the un-additized base oil. In the same way, in case of SDE-additized sample, the percent rise in service life of the base oil resulted was found to be 80.55 % and percent difference for KV obtained was found to be >70 % when compared with the un-additized sample. This nearly similar percent difference gained with the use of RHE and the SDE in terms of OSI and physico-

chemical analyses show the correlation of monitoring methods and pronounced effectiveness of antioxidants under study.

3.4.1.3. OSI Analysis of Various Base Oil Samples Oxidized at 200 °C for 06 Hours

To investigate the thermo-oxidative stability of the base oil and antioxidant effectiveness at elevated temperature, the conductance changes were measured for the samples under study after their oxidation at 200 °C. The graphs (oxidographs) between conductance vs time in case of un-additized, RHE- and SDE-additized base oil samples have been shown in Fig-3.46. The oxidographs contained normal lines representing useful normal service life and the abrupt lines indicating degradation time inverse of useful life of lubricant.

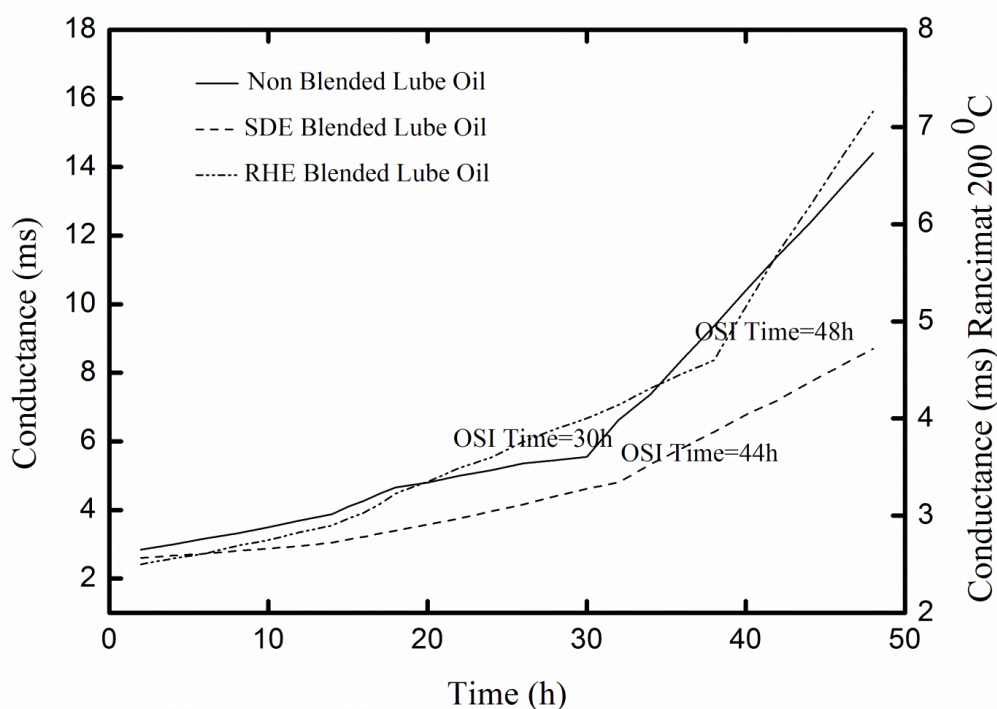


Fig-3.46. Oxidative stability index measurements for un-additized, RHE-additized and SDE- additized base oil samples oxidized at 200°C

Non blended base oil sample showed the normal conductance changes for the time duration between 1-30h as oxidation time which is clear from the normal straight line shown in Fig-3.46. The abrupt line appeared at 31st h and the conductance changes



were saved till 48th h. The percent difference in OSI time in case of the oxidized base oil between 100⁰C and 200⁰C determined was 20.0 %. Before OSI time, during the induction period the average per hour difference conductance calculated was found to be 0.065 ms and after it was 0.200 ms, respectively. Thus, per hour difference found to be more than the significant level due to larger rate of degradation at 200⁰C. Exposure of lubricant molecules to elevated temperature caused their cleavage involving C-C and C-H bonds scission that lead to larger amount of volatiles which in turn indicate increased level of quality declination. Therefore, level of degradation was found to be more prominent at 200⁰C than 100⁰C.

In case of the RHE-additized sample oxidized at 200⁰C, the normal conductance changes resulted for the period between 1- 47h as given in Fig-3.46 and indicated by normal line. Thus, induction period appeared to be above a straight line and found to be 47 h. It reveals the OSI time of 48h in case of the RHE-additized base oil oxidized 200⁰C as presented by an erect sharp line in Fig-3.46. The average difference in conductance per hour obtained was found to be 0.034 ms during induction period and after was 0.100 ms. The significant change of per hour difference of OSI data was converted into insignificant in the presence of RHE before OSI time that delayed the OSI time and thus enhanced the service life of the lubricant. Even after OSI time, per hour difference was reduced with RHE which reveals the declined the level of thermal degradation to a larger extent.

In the same way, in case of the SDE-additized sample, both normal and sharp lines were appeared which indicate induction period and OSI time as expressed in Fig-3.46. Normal conductance rise was seen for oxidation time between 1 – 43rd h which represents the induction period of oxidized base oil in the presence of the SDE at 200⁰C. After induction period, an abrupt line was observed at 44th h of oxidation suggested the OSI time for the SDE-additized sample at above conditions. In induction period, the per hour average difference in conductance obtained was 0.040 ms and after it was noted as 0.160 ms. Thus, SDE as well converted the per hour difference from significant to insignificant that increases useful lubricant life by delaying the OSI time. After OSI time,



per hour difference was further reduced which decreased the level of degradation especially at elevated temperature.

The OSI time resulted at 200⁰C was found to be 30 h in case of the un-additized base oil sample which is much lower than obtained at 100⁰C. It indicates that temperature rise has large impact on reduction of the useful service life of base oil as lubricant [55]. In presence of RHE and SDE, increment in OSI time occurred which were found to be 48 and 44h, respectively as clear from Fig.3.47.

The anti-oxidation evaluation in terms of SF values for RHE- and SDE-additized base oil samples oxidized at 200⁰C was determined. The SF value for the RHE-additized sample was found to be 160.0 and in case of the SDE was 146.67 as per data provided in Fig.3.48. Hence, it was confirmed that the percent difference in terms of OSI time brought with blending the base oil calculated in case of the RHE was 80.55 % and the SDE was 46.67 % as given in Fig-3.49. The service life in RHE-additized sample was enhanced to 48h and in case of SDE-additized sample to 44 h. Thus, improvement in service life of base oil at 200 °C achieved in the presence of the RHE as 80.55 % and in case of the SDE was 46.67 %. This performance of antioxidants under study indicated their excellent anti-oxidation potentials even at elevated temperature. Overall, the anti-oxidation performance of RHE and SDE was found to be outstanding at 100⁰C and excellent at 200⁰C.

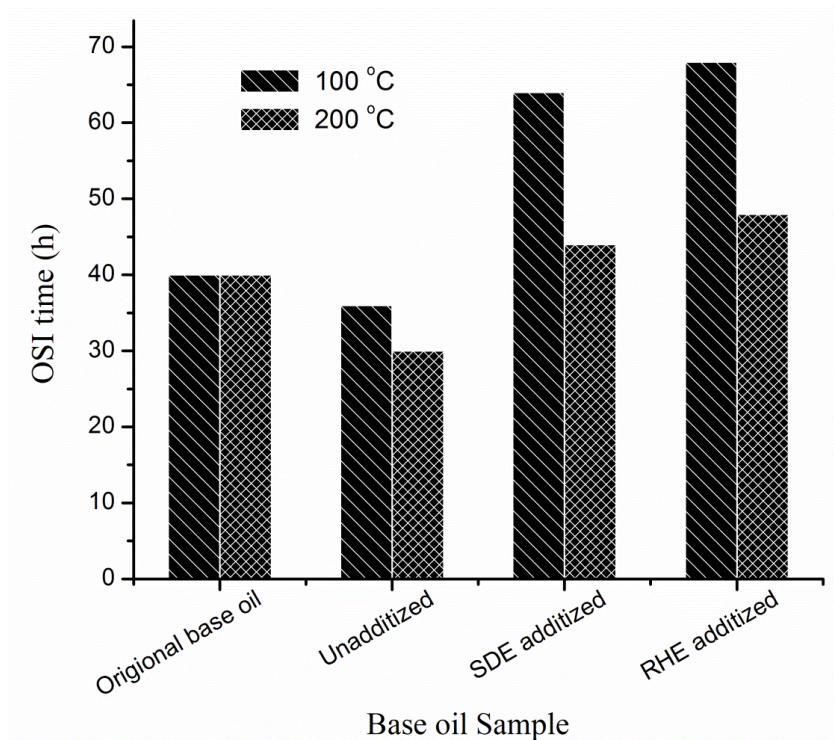


Fig-3.47. Comparison of OSI time measurements for un-additized, RHE- and SDE-additized base oil samples oxidized at 100⁰C and 200 °C

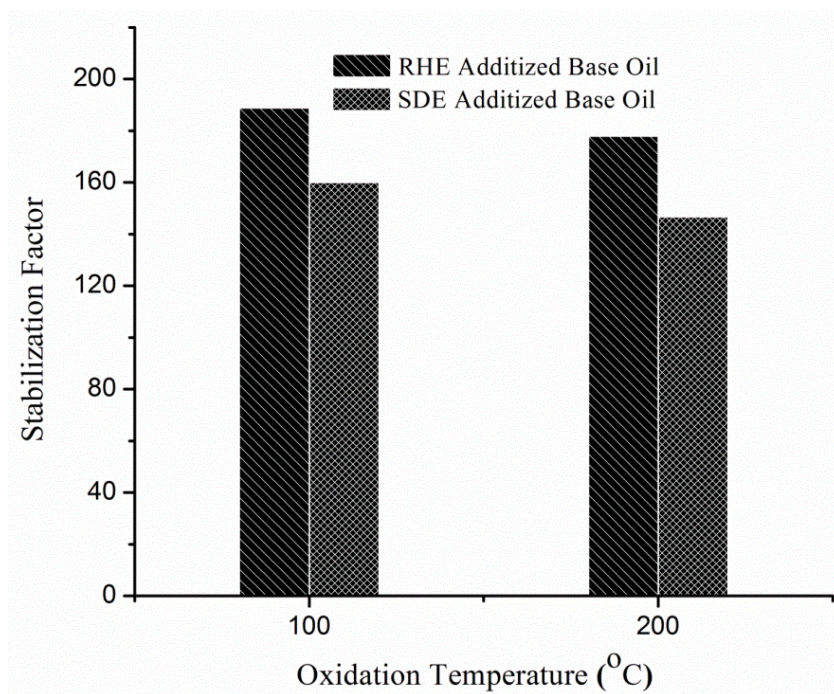


Fig.3.48. Comparison of stabilization factor for monitoring the antioxidant effectiveness of RHE- and SDE-additized base oil oxidized at 100 and 200 °C

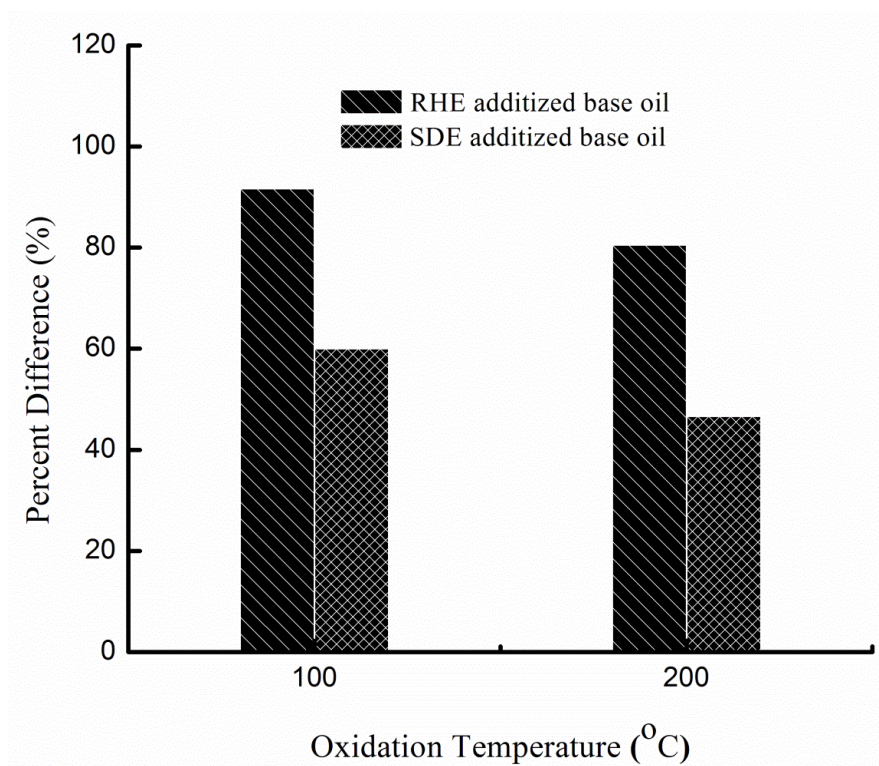


Fig-3.49. Comparison of percent difference of OSI time between RHE- and SDE-additized samples with un-additized base oil oxidized at 100 and 200°C



PHASE-V

Next to OSI analysis, thermo gravimetric (TGA) analyses in terms of T_{onset} , T_{offset} , mass loss as fast volatiles, and weight gain were performed in case of the un-additized and the additized base oil samples oxidized at 100 and 200 °C for time duration of 06 h in order to decide about the thermal antioxidant characters of the biomass derived oils. The results have been discussed in the proceeding section.

3.5. THERMOGRAVIMETRIC STUDY

The basic knowledge of the oxidative properties of lubricants is essential in order to investigate the long term thermal stability of these lubricants, which is a critically significant fluids property. Oxidation properties determined experimentally are often used to get aware of the actual lubricant service life at elevated temperatures and other extreme environment zones. More is the anti-oxidation potentials of lubricant to oxidation; less is the tendency it has to form deposits, sludge, and corrosive byproducts in engine and other industrial machinery services. The undesirable viscosity increases during service also associated with more resistivity to oxidation. The ASTM D943 test method is widely used in industry to assess long-term service oxidation stability and storage of oils in the presence of oxygen and nitrogen media.

To avoid time and chemicals consumption it has become necessary to seek development of new oxidation stability tests, which are able to represent field performance within a short testing time. Actually, thermo-analytical method i.e. thermogravimetric analysis (TGA) and DSC have got considerable attention [56]. The method provides a higher precision and sensitivity as well as use smaller amount of sample and the results are obtained faster compared to conventional methods. Thermogravimetric analysis (TGA) provides the analyst with a quantitative measurement of any change related with a transition. For instance, TGA can directly record the weight loss against temperature or time as a result of dehydration and decomposition of the oil. TGA is extensively used for analyzing both the thermal and oxidative stabilities of base and the engine oils. The physico-chemical changes are associated with dehydration, evolution of high and medium volatile decomposition products and cook disintegration.



Changes in weight are a result of the cleavage or formation of various physical and chemical bonds at high temperatures that lead to release of volatile products or formation of the heavier degraded products.

Generally, the evaporation losses of lubricant with temperature climb at a particular heating rate (10-20 °C/min) undertaken in three steps. In first step, the lower the primary products of degradation like peroxides, hydro-peroxides, alcohols, aldehydes, ketones, carboxylic acids, esters or lower hydrocarbons of lubricant get decomposed at temperature range of 100-250 °C. The second step involve the disintegration of the remained hydrocarbons as major constituent of lubricant (main body of lubricant) occurring at temperature limit of 250-400 °C. While the secondary products of degradation include the carbon residue (soot or cook), sludge, varnish, etc. undergo breaking at elevated temperature range of 400-800°C.

3.5.1. Thermal Analysis of RHE, SDE, Original (un-oxidized), and Various Oxidized Base Oil Samples

3.5.1.1. Thermal Analysis of RHE and SDE

Thermal Analysis of RHE

TGA profile determined in case of the RHE is given in Fig 3.50 and the related thermal analysis data is provided in Table 3.9. The results show a mass loss of the RHE at five different temperatures which indicate the presence of many different compounds in crude mixture form. Thus, five degradation steps were observed related to the oxidative and thermal decomposition of the different compounds as antioxidants. These TGA steps used to characterize the evaporation loss, thermal decomposition and combustion properties of the RHE.

The T_{onset} (initial temperature of degradation) obtained was 100°C and the T_{offset} (Final degradation temperature) was 149°C with sample loss of 05 % in O₂ environment. Similarly, in the presence of N₂, the T_{onset} was appeared to be 105°C and T_{offset} to be 160°C. First step is a minor one involved the evaporation losses of alcohols, aldehydes,



ketones and carboxylic acids of low molecular weight having non-antioxidant nature [57]. The results indicate the presence of these constituents in trace amount in the RHE.

In the 2nd degradation step, T_{onset} and T_{offset} in O_2 medium were found to be 150°C and 221°C with 60 % mass loss while in N_2 , these were found to be 161°C and 226°C with the same mass loss (60%), respectively. It might be due to the thermal decomposition of hydro-quinone, phenol, bromophenol, amine phenol, p-cresol, anisol, methoxy benzaldehyde, stearic acid, ascorbic acid, citric acid, etc. as antioxidant [58, 59, 60, and 61]. The results indicated the presence of these antioxidants in RHE in 60 % concentration. The presence of all these antioxidants has also been confirmed by GC-MS analysis of the RHE (Phase-VII).

The 3rd step of degradation event range in O_2 and N_2 presence was 222 -232 °C and 227 -237°C, involved 07 % mass loss as T_{onset} and T_{offset} , respectively. This degradation temperature range may be attributed to dihydroxy benzene, dihydroxy benzoquinone, pyrogallol (trihydroxy benzene) as antioxidant [62]. The RHE contains these constituents in concentration of about 07 % as clear from the mass loss data.

The major loss of sample mass about 72 % happened at temperature range of 150-221 °C which shows that RHE mainly comprised of phenols and their derivatives including alkylated phenols, hydroxyl phenols, amine phenols, etc. Thus, compounds that volatilized or thermally decomposed in the temperature range of 100-221°C resulted in high volatile matter of the extract. While others that degraded at temperature range of 222- 350°C are medium volatiles and the rest is char that combusted above 350°C.

The 4th one is a medium step involved the mass loss of about 12 % of the sample. The T_{onset} was found to be 233°C and 252°C, and T_{offset} was 238°C and 259°C in O_2 and N_2 environments, respectively might be due to the thermal splitting of α -tocopherol, naphthalene diol and hydroxy quinoline as antioxidant as reported earlier [63, 64, 65].

The 5th minor step is medium one as well that assigned to the thermal scission of 7-hydroxy, 4-methyl coumarine, benzoyl phenyl hydroxyl amine, nitro and nitroso naphthol [66]. RHE under study exhibited 13 % mass loss corresponded to the presence of



these constituents for which T_{onset} observed were; 253°C and 315°C while 260°C and 327°C as T_{offset} in O_2 and N_2 atmospheres, respectively

The remaining residue left was heavy that had undergone combustion with mass loss of 03 % in the last 6th step of thermal operation. It was initiated at temperature of 316°C and the whole mass get vanished at 400°C in O_2 presence and under N_2 combustion of char recorded was found to be 328°C and completed at 400°C.

The above analysis indicates that RHE is a rich source of natural antioxidants like phenolic compounds, hydroquinone, pyrogallol, alpha tocopherol, coumarin, etc. that show high oxidative and thermal stability. It leads to the suitability of RHE to be used as natural antioxidant.

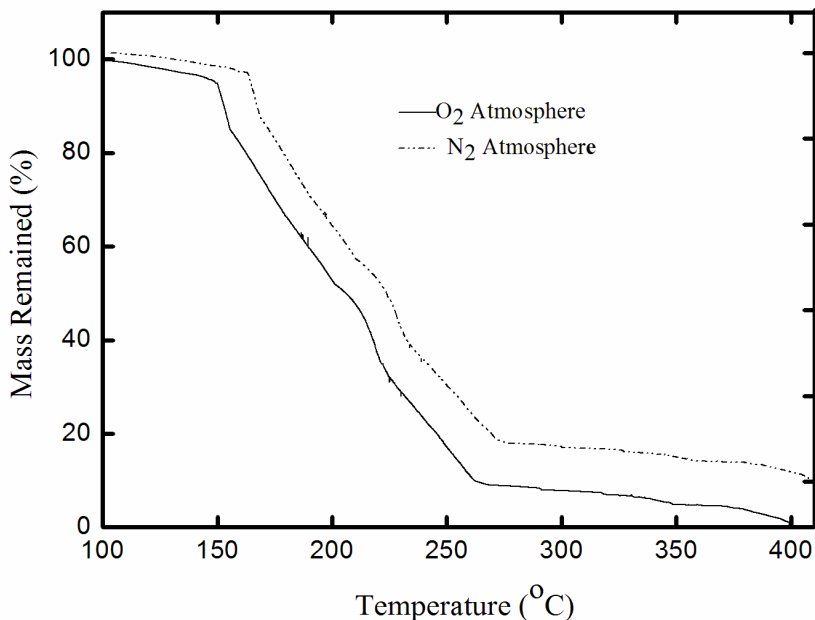


Fig.3.50. TGA profile of original RHE in O_2 and N_2 atmospheres

**Table: 3.9. TGA Thermo-oxidative Degradation Data of the Original RHE Under Oxygen and Nitrogen Atmospheres**

Antioxidant	Treatment Environment	Degradation steps	T Onset (°C)	Mass Left befor deg. Step (wt %)	T Offset (°C)	Mass Left after deg. step (wt %)	Mass lost per deg. Step (wt %)
RHE	O₂	1	100	100	149	95	05
		2	150	95	221	35	60
		3	222	35	232	28	07
		4	233	28	252	16	12
		5	253	16	315	03	13
		6	315	03	336	00	03
RHE	N₂	1	105	100	160	95	05
		2	161	95	226	36	59
		3	227	36	237	28	08
		4	238	18	259	15	13
		5	260	15	327	03	12
		6	328	03	341	00	03



Thermogravimetric Analysis of SDE

TGA study of the SDE was also performed, the profile is provided in Fig. 3.51 and the thermal analysis data is depicted in Table 3.10.

A significant reduction in mass of the SDE was observed at about five points of temperature which reveal the presence of five different types of substances in impure form. Thus, oxidative and thermal deterioration of the sample occurred at various temperatures given by several disintegration steps.

Similar to the first degradation step of the RHE, in case of the SDE, the volatile loss occurred at temperature range of 105-171°C. This loss may be due to evaporation of alcohols, aldehydes, ketones, carboxylic acids, etc. [67]. The T_{onset} and T_{offset} recorded were found to be 100°C and 155°C and 107°C and 171 °C with mass loss of 06 % in oxidative and thermal degradation, respectively.

The 2nd step is major one which involved the 65 % of mass loss. This may be due to the thermal breaking of the phenolic antioxidants. In case of oxidative degradation, the T_{onset} obtained was 156°C and T_{offset} was 226°C while in thermal one, the T_{onset} found was 172 °C and T_{offset} was 244°C. The antioxidants frequently decomposed in this step are reported to be naphtho quinone, ascorbic acid, phenols, methyl phenols, amine phenol, bromo phenol, methoxy phenols (anisol) etc. [59, 60, 61, 67, 68, 69, 70]. The results indicate their presence as confirmed by the subsequent GCMS analysis.

The 3rd step is medium one which involve the thermal splitting of one of the excellent antioxidant pyrogallol (1, 2, 6- trihydroxy benzene), & naphthalene diols, and alkylated benzene diol nitro-naphthol & methyl phenyl acetamide [62, 64, 66] showing a mass loss of about 20 % indicating their presence in SDE. In O₂ environment, the initial degradation temperature found was 227 °C and terminal degradation temperature was 246°C and in N₂ medium, T_{onset} was 245°C and T_{offset} was 264°C

In the 4th step of oxidative environment and inert atmosphere, the T_{onset} found were 247°C and 265°C and the T_{offset} were 297°C and 317°C, respectively. This step was due to the thermal decomposition of 7-hydroxy, 4-methyl coumarin and phenyl azo b-

naphthol in the SDE [59, 63,64] with mass loss of 6% reveal its concentration in the bio mass extract under study.

The last 5th step involve the combustion of fixed carbon or carbon residue of the SDE for which the T_{onset} and T_{offset} recorded in O_2 and N_2 media were 298°C and 318°C and 400°C, respectively with mass loss of 03 %.

Thermal analysis of the SDE showed that it is composed of high volatile matter (06 %), thermally stable phenol derived antioxidants below 200 °C (65 %) and other thermally stable natural antioxidants (20 %) above 200°C as medium volatiles. The natural thermally stable antioxidants found were phenolic compounds including naphtho quinone, alkylated hydroquinone, anisole pyrogallol and coumarin in high concentration. Thus, the SDE can be employed as an additive of natural antioxidants in base oil because of the presence of abundant excellent antioxidants.

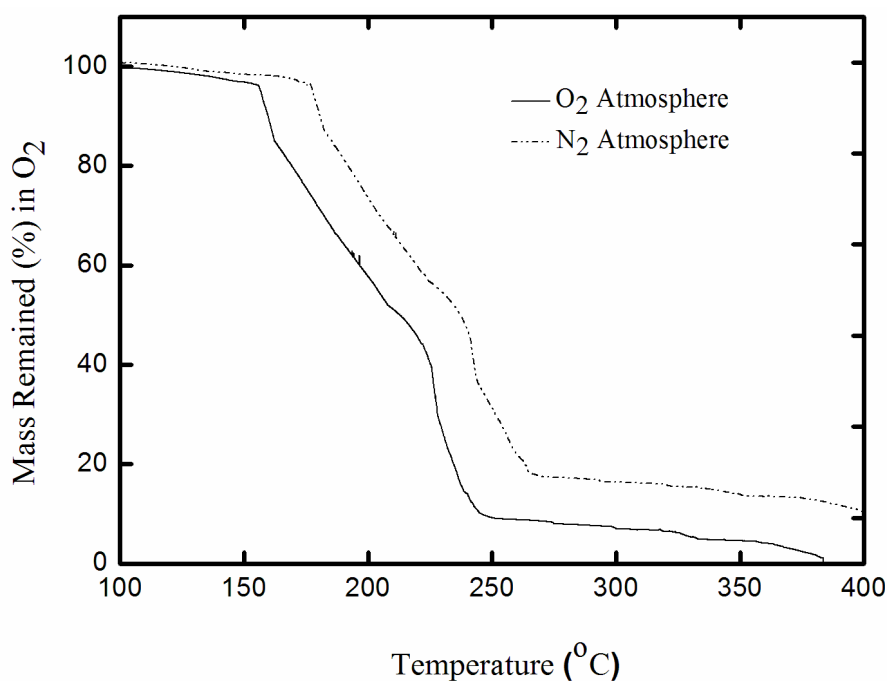


Fig.3.51. TGA profile of original SDE in O_2 and N_2 atmospheres

**Table: 3.10. TGA Thermo-oxidative Degradation Data of the Original SDE Under Oxygen and Nitrogen Atmospheres**

Antioxidant	Treatment Environment	Degradation step	T Onset (°C)	Mass left before deg. step	T Offset (°C)	Mass left after deg. step (wt %)	Mass lost per deg. step (wt %)
SDE	O₂	1	100	100	155	94	06
		2	156	94	226	29	65
		3	227	29	246	09	20
		4	247	09	297	03	06
		5	298	03	400	00	03
SDE	N₂	1	100	100	171	95	05
		2	172	90	244	30	65
		3	245	30	264	10	20
		4	265	10	317	03	06
		5	318	03	400	00	03

3.5.1.2. Thermal Analysis of Original Base Oil Samples (un-oxidized)

The original base oil sample was thermo-oxidatively evaluated using the mass loss in O₂ and in N₂ atmospheres which is associated with evaporation losses and decomposition of the oil under test. The degradation steps of oil was observed by TGA (thermo-gravimetric Analyzer) as TG curve can provide useful data about mass loss with temperature at which these events are most significant termed as thermogram or TG profile. The mass loss in N₂ presence reflects the evaporation and decomposition losses of oil and O₂ atmosphere determine the oxidative and thermal stability of the oil sample. In O₂ and N₂ atmospheres, oxidative and thermal stability of lubricant is assessed where mass loss found to be a function of temperature [71].



Thermogravimetric analysis data determined in case of the original un-oxidized base oil sample including degradation steps, onset-offset temperatures, mass remained before and after each thermal degradation step and total mass lost per step of degradation is provided in Table 3.11. In thermal analysis, mass loss of sample is determined against the temperature in nitrogen and oxygen atmospheres. Oxidative stability is investigated in the presence of oxygen and thermal one in nitrogen environment. The lubricant is more stable which withstand elevated temperature and do not get pyrolyzed in O_2 and in N_2 atmospheres. Each TG profile which is the plot between mass remained of lubricant against the temperature for the original un-oxidized base oil are provided in Fig. 3.52.

Three main steps were detected in the degradation of the base oil containing major and minor ones. The T_{onset} (initial temperature of degradation) and T_{offset} (terminal degradation temperature) were observed for all the three steps.

The T_{onset} noted from the profile was $100^\circ C$ and T_{offset} was $230^\circ C$. The thermogram shows a 10 % mass loss in the first minor step of O_2 atmosphere. For the same mass loss determined in N_2 medium, the T_{onset} was found to be $100^\circ C$ and T_{offset} $248^\circ C$. This mass loss can be corresponded to the volatile loss of either lower paraffinic hydrocarbon.

The mass loss started from 11 % and continued upto 96 % in O_2 atmosphere in the 2nd step involved 86 % loss in this major step. T_{onset} seen was $231^\circ C$ which vanished at $390^\circ C$. In case of thermal degradation (N_2 environment), T_{onset} was found to be $249^\circ C$ and T_{offset} was $411^\circ C$ for the same (86%) mass loss. Actually, this significant mass loss was probably due to the degradation of the paraffinic hydrocarbons present as main ingredient in the base oil.

In the 3rd step, the T_{onset} appeared to be $391^\circ C$ and T_{offset} to be $596^\circ C$ because of the charring of the fixed carbon or carbon residue involving 03 % mass loss. In the thermal decomposition step, the T_{onset} determined was $412^\circ C$ and T_{offset} was $611^\circ C$ with the same mass loss. The remaining 01 % mass may be due to the ash content of the base oil.

Base oil oxidation depends on its origin from which it is obtained. Base oil stability concerned with its nature whether synthetic or mineral, hydrocracking, solvent nature (neutral, acidic or basic), and also on their response to the antioxidant treated [72]. The 2nd step is the real quality assessment one for which T_{onset} is generally found below 200 °C. But in case of base oil under test, T_{onset} was found to be 230 °C which indicate its high thermo-oxidative stability of the base oil [73].

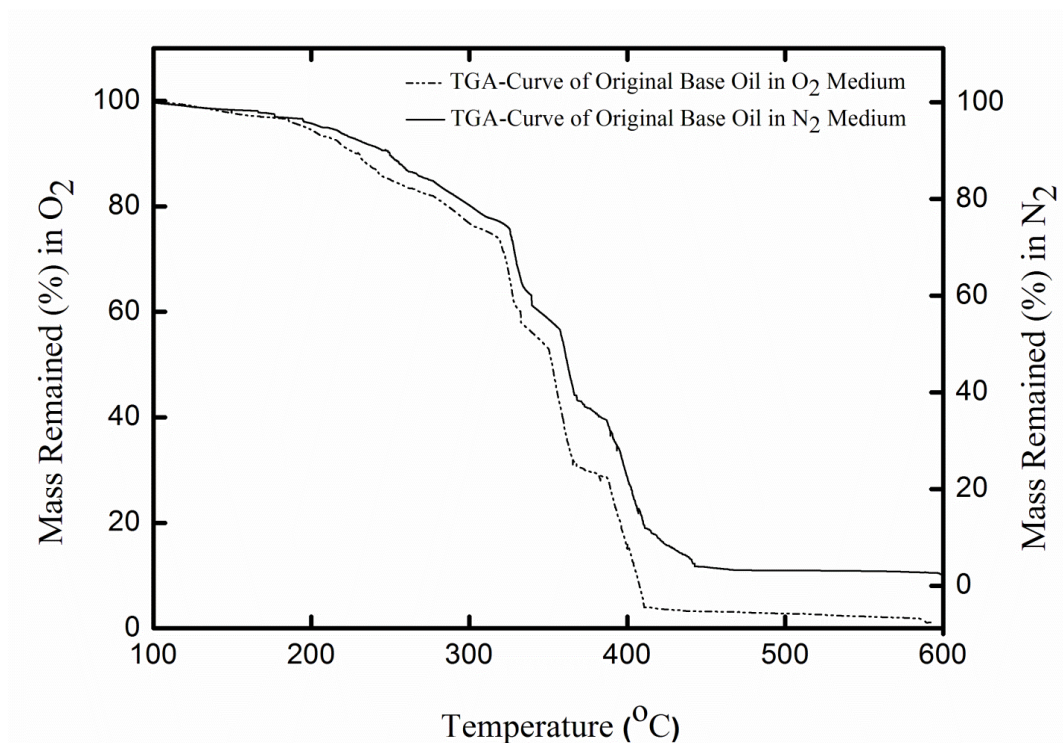


Fig.3.52. TGA profile of original base oil in O₂ and N₂ atmospheres

**Table: 3.11. Thermo-Oxidative Degradation Data of the Original Base Oil Under Oxygen and Nitrogen Atmospheres**

Treatment Environment	Degradation Step	T Onset (°C)	Mass left before deg. step (wt %)	T Offset (°C)	Mass left after deg. step (wt %)	Mass lost per deg. step (wt %)
O ₂	1	100	100	230	90	10
	2	231	90	390	04	86
	3	391	04	596	01	03
N ₂	1	101	100	248	90	10
	2	249	90	411	04	86
	3	412	04	611	01	03

3.5.1.3. Thermal Analysis of Various Base Oil Samples Oxidized at 100°C for 06 Hours

The TG profiles of the un-additized, the RHE-& SDE additized based oil samples oxidized at 100°C for 06 h are provided in Fig.3.53-Fig.3.55 and the related thermal data is provided in Table 3.12. Thermo-oxidative stability of the samples under study was evaluated in terms of change in T onset, concentration of primary degradation products and weight gain.

The T onset appeared for the un-additized oxidized base oil sample in O₂ presence (oxidative degradation) was found to be 205°C and in N₂ atmosphere was 230 °C. In case of the RHE-additized base oil, the T_{onset} obtained was found to be 228°C in O₂ presence and 248 °C in N₂ atmosphere. While in case of the SDE-additized sample, T_{onset} was 224 °C and 244 °C in O₂ and N₂ environments, respectively as clear from the Fig.3.56. The results indicated that the RHE and SDE caused appreciable increment in the T_{onset}. It is because higher the T_{onset} for a substance better will be its antioxidant behavior as reported elsewhere [4].



Percent difference determined in case of the un-additized base oil and its blends with the RHE and SDE after oxidation at 100 °C in comparison with the original (un-oxidized) base oil was determined in order to monitor the extent of degradation and the performance of antioxidants under test [74]. The percent differences in T_{onset} calculated in case of un-additized base oil after oxidation with respect to the original (un-oxidized) base oil were found to be 12.19% and 7.82% in thermal and oxidative degradation, respectively as per data given in Fig 3.57. The percent difference in case of un-additized sample with respect to control is quite higher which indicate significant level of thermo-oxidative degradation of un-additized base oil. The use of the RHE and SDE as antioxidants reduced the percent difference to a greater extent which showed their excellent antioxidant character. The percent differences determined in case of the RHE-additized MBO were found to be 0.87 % and 0.0 % and the SDE were 2.67 % and 1.63 % in O_2 and N_2 atmospheres, respectively. Percent differences determined in comparison with the original base oil in both oxidative and thermal degradations followed the order;

$$\text{RHE-additized MBO} < \text{SDE additized MBO} < \text{un-additized MBO}$$

The percent differences in case of the additized samples are very low which is almost close to the original base oil value reveal the outstanding antioxidant behavior of the RHE. While in case of the SDE-additized sample, the values are quite small evaluate its excellent antioxidant performance.

Degree of degradation can also be evaluated from the concentration of the fast volatiles as mass loss in 1st degradation step. In case of the un-additized base oil, fast volatiles were found to be 12 % in both O_2 and N_2 environments. In case of the RHE- and SDE-additized MBO samples, the fast volatiles resulted was 10 % in both oxidative and thermal degradation of samples under study as per data provided in Fig.3.58. Thus, the RHE and SDE reduced the fast volatiles by 02 % than the oxidized lube oil which indicate their effectiveness as antioxidants.

Weight gain during oxidative degradation is observed in the last step of degradation which can be used as marker of degree of degradation. The mass loss determined in case of un-additized and additized samples was compared with the original

(un-oxidized) base oil as per results given in Fig.3.59. Percent decrease in mass loss in additized oil samples showed the performance of antioxidant [75]. The mass loss found in case of un-additized MBO oxidized at 100 °C was found to be 05 %. The weight gain appeared was significant which indicate the significant extent of thermo-oxidative degradation of base oil. While mass loss in case of both RHE and SDE blends in the last step of oxidative degradation obtained was found to be 02%. It implies that both antioxidants of biomass extracts have worked efficiently in minimizing the weight gain. Rather the mass loss found was equal to that obtained in case of the original oil which indicates negligible degradation of the base oil in the presence of the RHE and SDE.

The above indicators of thermogravimetric analysis inferred the outstanding antioxidants character of the RHE and SDE in their blends at 100 °C.

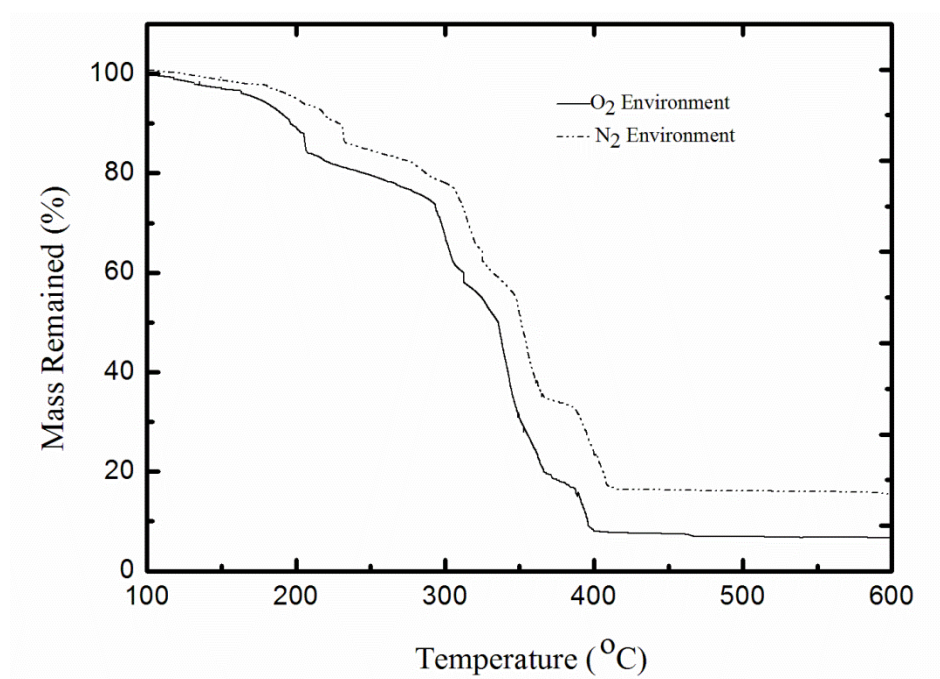


Fig.3.53. TGA profile of un-additized base oil oxidized at 100 °C

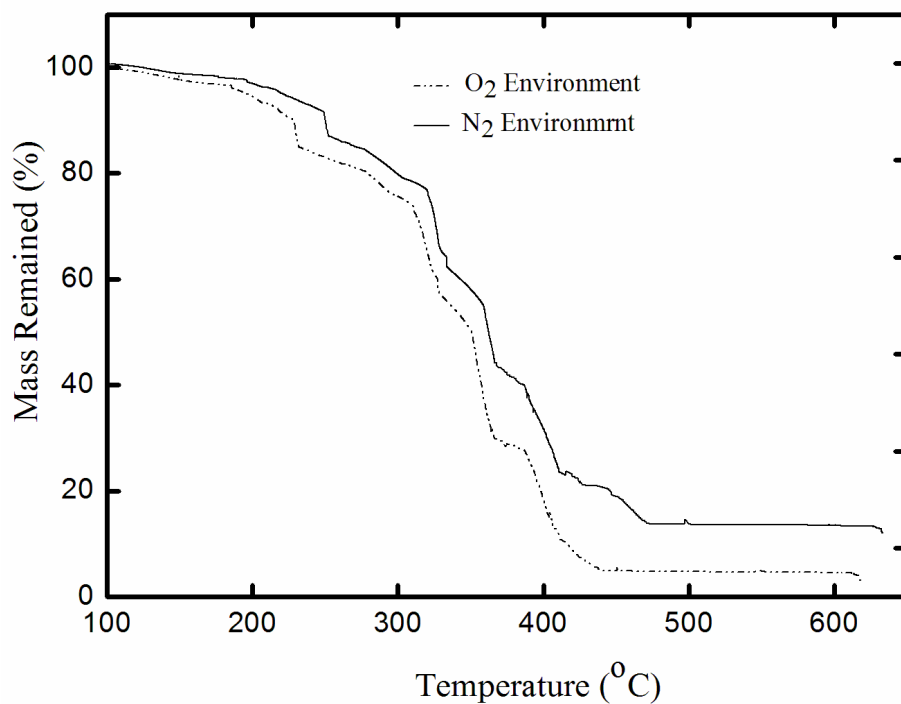


Fig. 3.54. TGA profile of RHE- additized base oil oxidized at 100 °C

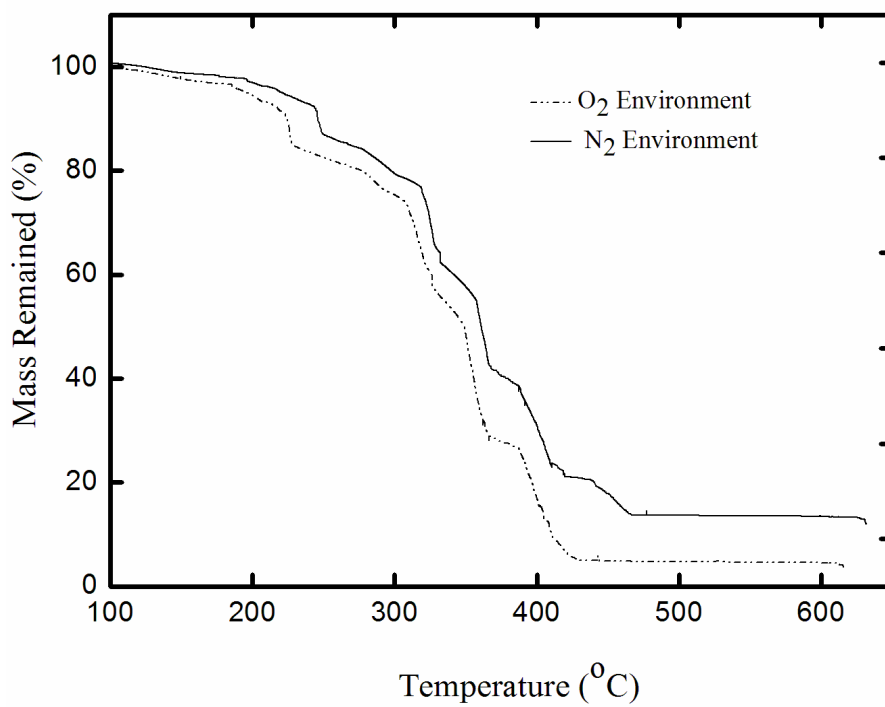


Fig.3.55. TGA profile of SDE-additized base oil oxidized at 100 °C

**Table: 3.12. Thermo-oxidative Degradation Data of Un-additized, RHE-and SDE-additized Base Oil Samples Oxidized at 100 °C**

Sample	Atmosphere	Degradation steps	T Onset (°C)	Mass left before deg. step (wt %)	T Offset (°C)	Mass left after deg. step (wt %)	Mass lost per deg. step (wt %)
Un-additized Oxidized Base oil	O ₂	1	100	100	205	88	12
		2	206	88	400	08	80
		3	401	08	627	03	05
	N ₂	1	100	100	230	88	12
		2	225	89	415	08	80
		3	416	08	642	03	05
RHE-Additized Oxidized Base oil	O ₂	1	100	100	228	90	10
		2	229	90	440	05	85
		3	441	05	618	03	02
	N ₂	1	100	100	248	90	10
		2	249	90	473	05	85
		3	474	05	633	03	02
SDE-Additized Oxidized Base	O ₂	1	100	100	224	90	10
		2	225	91	430	05	88
		3	431	05	616	03	02
	N ₂	1	100	100	244	90	10
		2	245	94	466	05	85
		3	467	05	631	03	02

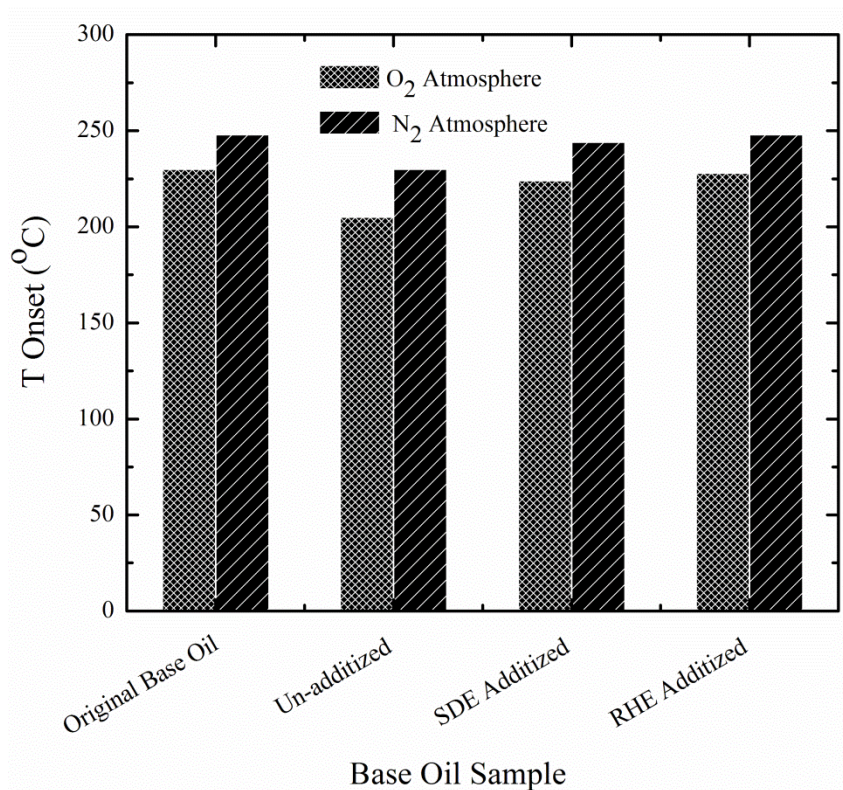


Fig.3.56. Comparison of T_{onset} of un-additized, SDE-and RHE-additized base oil samples oxidized at 100 $^{\circ}C$ with control sample

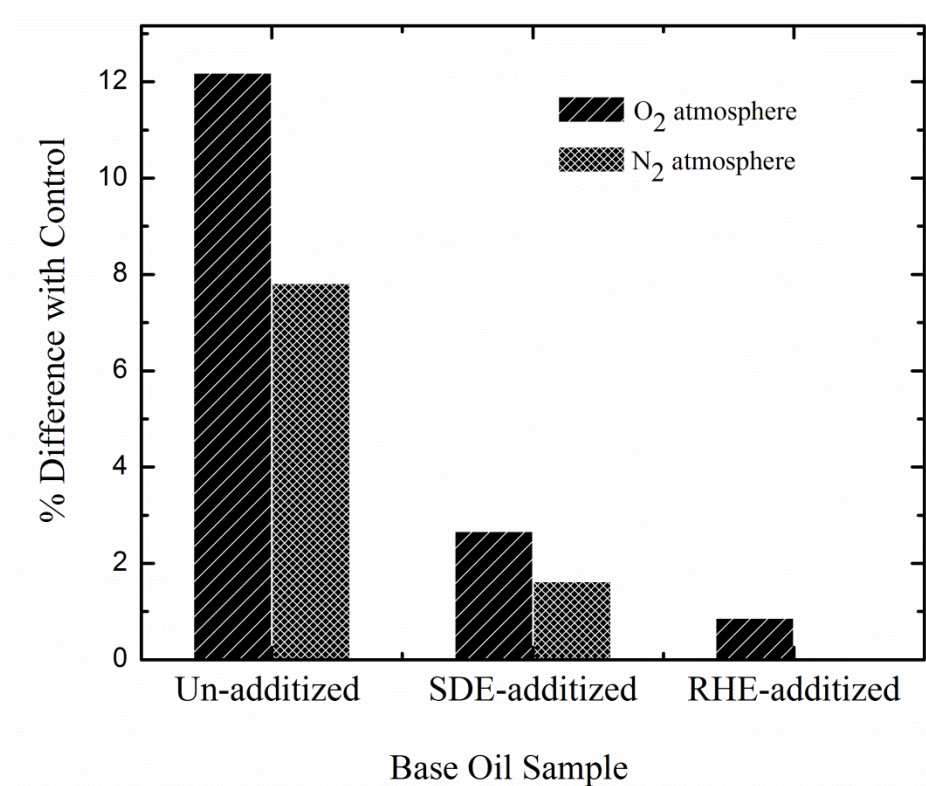


Fig.3.57. Comparison of percent difference of T_{onset} of un-additized, SDE- and RHE-additized oxidized base oil samples oxidized at 100 °C with control sample

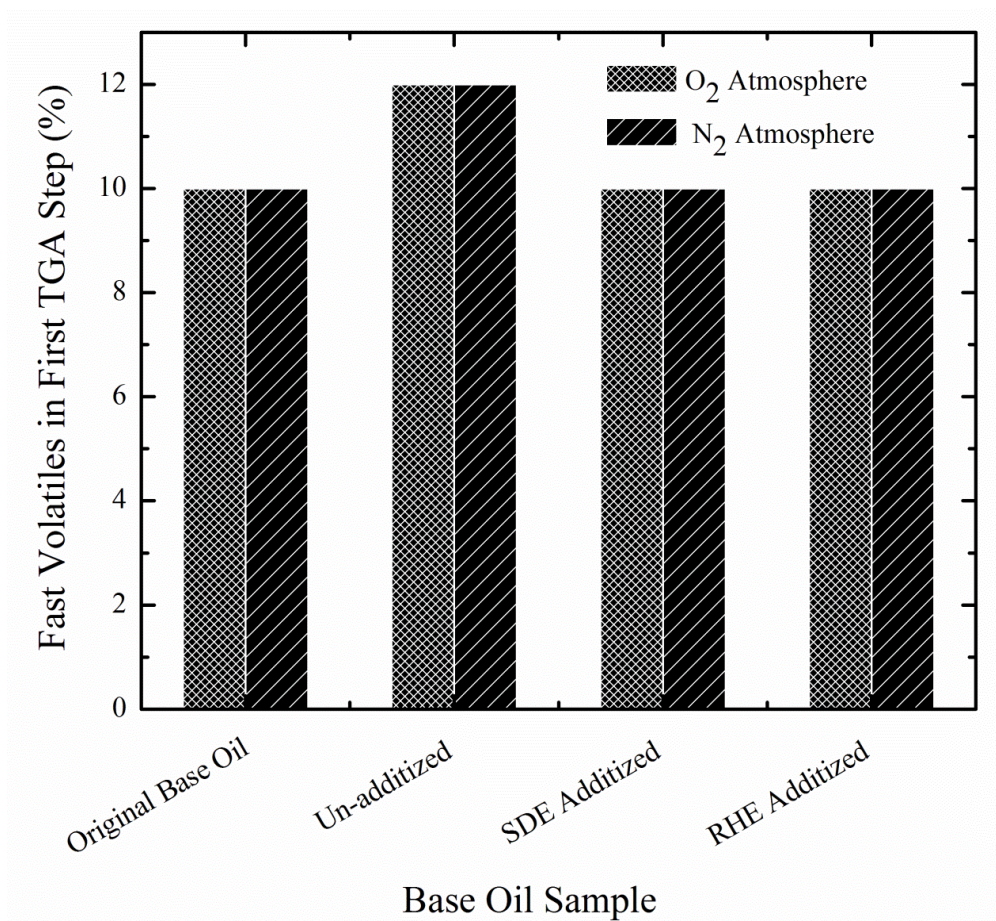


Fig.3.58. Comparison of fast volatiles of un-additized, RHE-and SDE-additized base oil samples oxidized at 100 °C with control sample

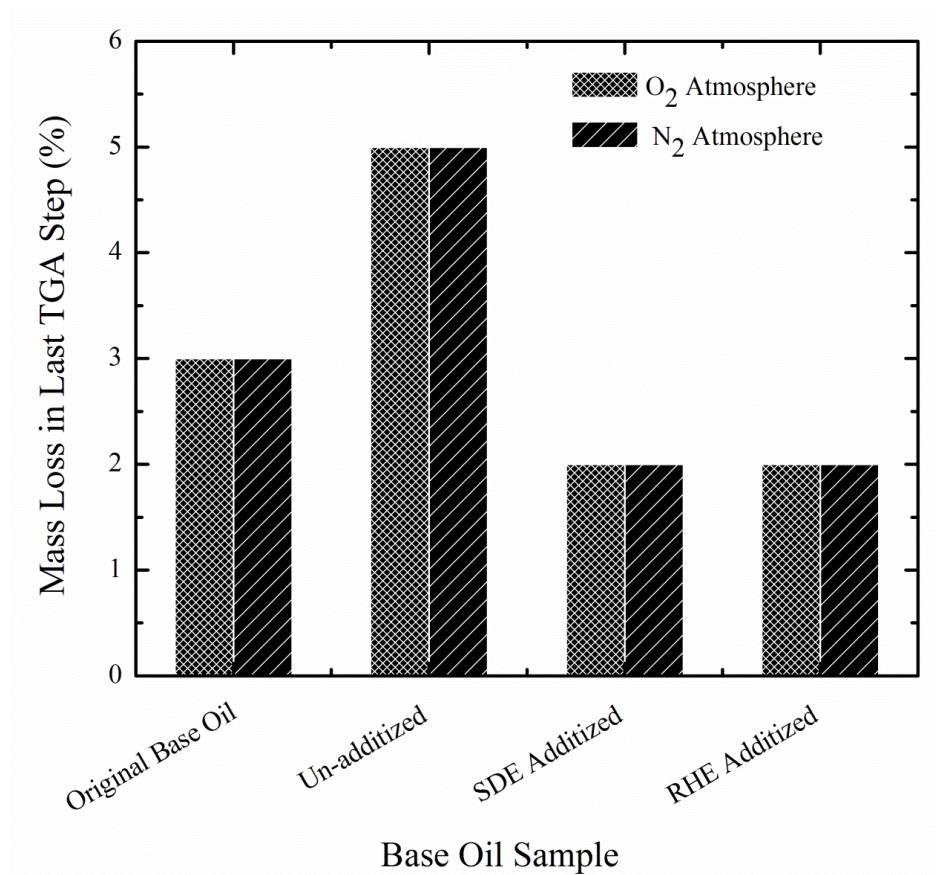


Fig.3.59. Comparison of weight gain of un-additized, RHE- and SDE-additized base oil samples oxidized at 100 °C with control sample

3.5.1.4. Thermal Analysis of Various Base Oil Samples Oxidized at 200°C for 06 Hours

Thermal analysis of the base oil samples (un-additized, RHE-&SDE- additized) oxidized at 200°C for 06 h was also performed. The corresponding TG profiles of oxidative (O₂)&thermal degradations (N₂) are provided in Fig. 3.60, Fig.3.61 and Fig.3.62 and the related thermogravimetric analysis data is given in Table-3.13, respectively.

In TGA evaluation of the base oil samples at 200 °C, the parameters like T_{onset} , fast volatile losses and weight gain were focused in order to investigate the level of degradation and the extent to which RHE and SDE antioxidants are efficient. In case of the un-additized, RHE- and SDE-additized samples, the T_{onset} obtained in O₂ environment were observed to be 180 °C, 210 °C and 204 °C, respectively as can be seen



from TGA profiles given in Figs 3.60, 3.61 and 3.62 [76]. The comparison of the T_{onset} for the various oxidized base oil samples with control sample in O_2 and N_2 atmospheres is shown in Fig. 3.63 which indicated efficacy of RHE and SDE as antioxidant. The results clearly evaluate oxidative and thermal stabilities of the base oil in presence of the RHE and SDE. Effective antioxidants usually enhances the T_{onset} 20-30 °C in blended form in base oil [77, 78] as caused by RHE and SDE in oil under test. The T_{onset} in N_2 atmosphere determined in case of the un-additized MBO, RHE-and SDE-additized base oil samples oxidized at 200 °C were found to be 207, 221 and 218 °C, respectively.

The percent difference in T_{onset} as compared with the fresh original base oil calculated in case of un-additized, RHE- and SDE-additized samples were observed to be 27.77 %, 9.52 % and 12.74 %, respectively as provided in Fig.3.64. Similarly, in thermal degradation, the T_{onset} percent differences with respect to the original oil obtained were found to be 19.80, 12.21 and 13.76 %, respectively as illustrated in Fig 3.64. Percent difference found in case of both of oxidative and thermal degradations followed the order;

$$\text{RHE-additized MBO} < \text{SDE -additized MBO} < \text{un-additized MBO}$$

Fast volatiles in 1st step of degradation determined in case of the un-additized, RHE-and SDE-additized were measured and inter-compared. Fast volatiles observed from TGA profile (Fig.3.65) in case of un-additized MBO was found to be 15 % as determined in both oxidative and thermal degradation studies. While in case of RHE-and SDE-additized samples, the fast volatiles observed to be 10 % in both oxidative and thermal deterioration. Thus, reduction in the fast volatiles caused by RHE and SDE was about 05 % keeping in view 15 % of the total difference which showed their effective antioxidants behavior at 200 °C.

The weight gain changes that occurred in last oxidative degradation step were also determined. Actually, weight gain occurred due to the addition of atmospheric oxygen (O_2) as extra mass in the oxidized products as a result of thermo-oxidative degradation. The weight gain appeared in the form of mass loss in the last oxidative degradation step in comparison with that of original oil is presented in Fig.3.66. In case of un-additized



sample, the mass loss seen at 200 °C was 09 % in both O₂ and N₂ atmospheres, respectively. The weight gain observed was significant when compared with that of the original base oil which was 02 %. This larger weight gain might be due to the formation of polymeric oxidized resinous products via oxidation of the base oil. In case of RHE and SDE blends, the mass loss obtained was 04% in both O₂ and N₂ media. It indicated the more prominent degradation occurred in the absence of antioxidants under study which is made insignificant in the presence of biomass extracts as antioxidants. The insignificant value of the weight gain in the presence of antioxidants attributed to insignificant degradation which shows the effectiveness of the RHE and SDE as antioxidants. It infers that both antioxidants have proved their anti-oxidation capabilities in overcoming the weight gain.

These thermogravimetric analysis indicators conclude the excellent antioxidants potentials of RHE and SDE in their blends by extending T onset to larger value, lowering the volatiles loss and reducing the weight gain at 200 °C.

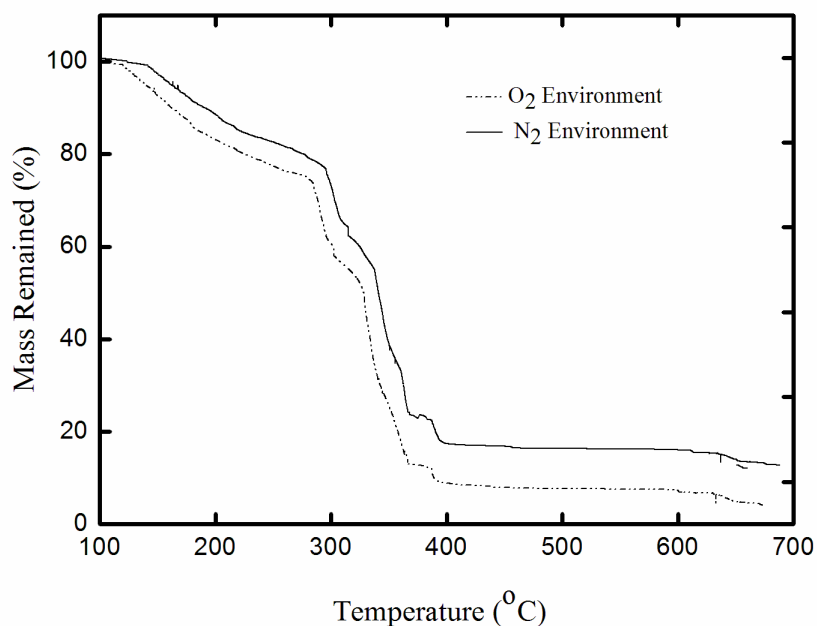


Fig.3.60.TGA profile of un-additized base oil oxidized at 200 °C

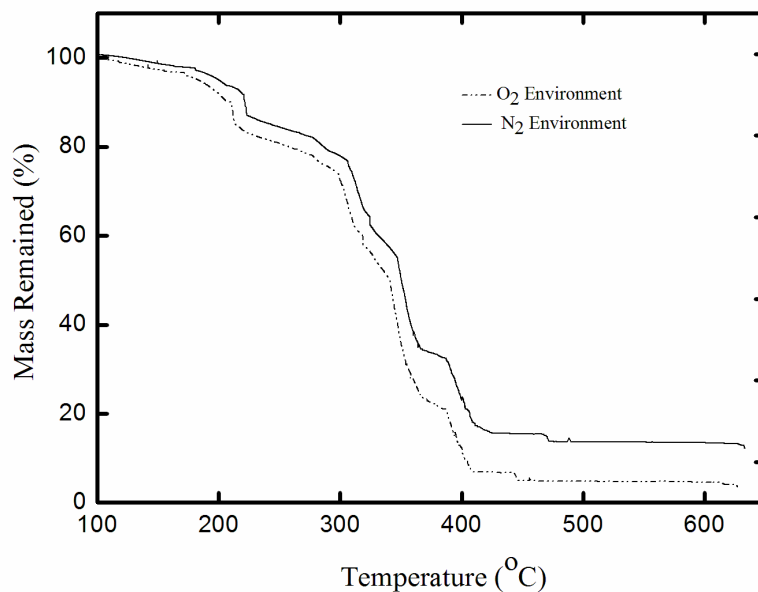


Fig.3.61.TGA profile of the RHE- additized base oil oxidized at 200 °C

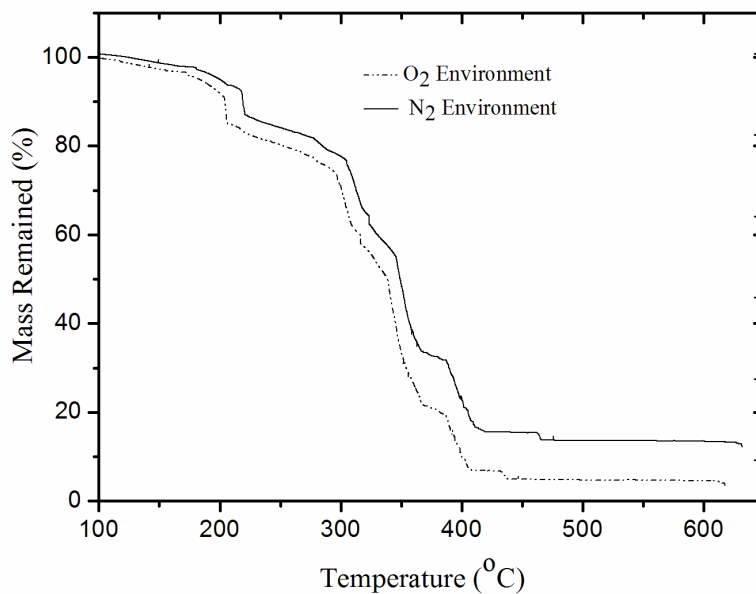


Fig. 3.62.TGA profile of the SDE- additized base oil oxidized at 200 °C



Table: 3.13. Thermal Degradation Data Under Oxygen and Nitrogen Atmospheres of the Un-additized, the RHE-and the SDE-additized Base Oil Samples Oxidized at 200°C

Sample	Treatment Atmosphere	Degradation step	T Onset (°C)	Mass left before deg. step (wt %)	T Offset (°C)	Mass left after deg. step (wt %)	Mass lost per deg. step (wt %)
Un-additized Oxidized Base oil	O ₂	1	100	95	180	85	15
		2	181	85	368	13	72
		3	369	13	675	04	9
	N ₂	1	100	100	207	85	15
		2	208	85	389	13	72
		3	390	13	688	04	09
RHE- Additized Oxidized Base oil	O ₂	1	99	98	210	90	10
		2	211	90	408	07	83
		3	410	07	627	03	04
	N ₂	1	100	100	221	90	10
		2	222	90	424	07	83
		3	425	08	633	03	04
SDE-Additized Oxidized Base	O ₂	1	100	97	204	90	10
		2	205	90	406	07	83
		3	407	07	617.5	03	04
	N ₂	1	100	100	218	90	10
		2	219	90	419	07	83
		3	420	08	632	03	04

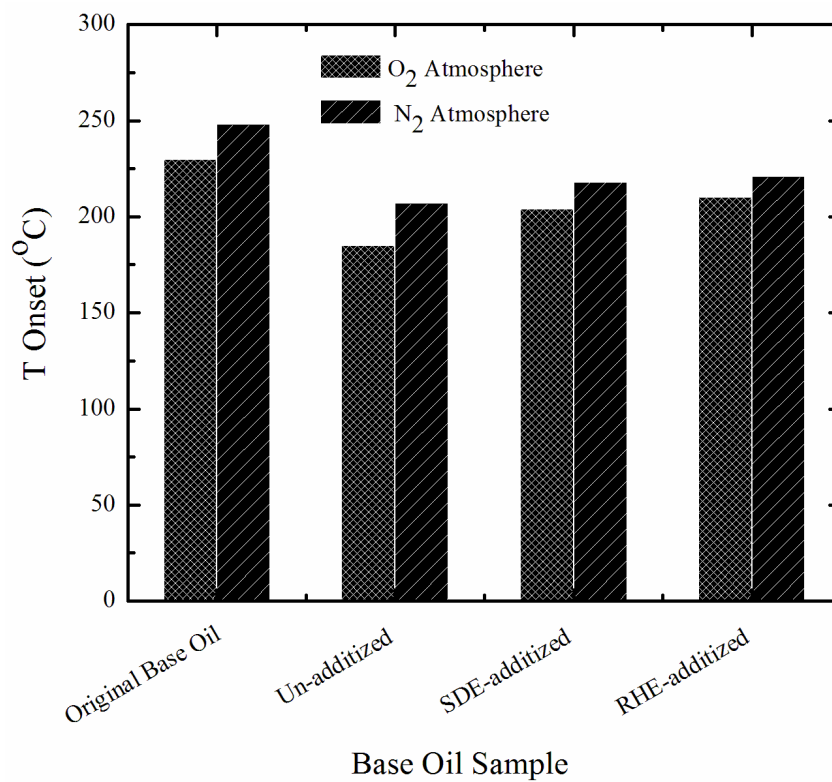


Fig.3.63. Comparison of T_{onset} of the un-additized, RHE- and SDE- additized base oil samples oxidized at 200 °C with control sample

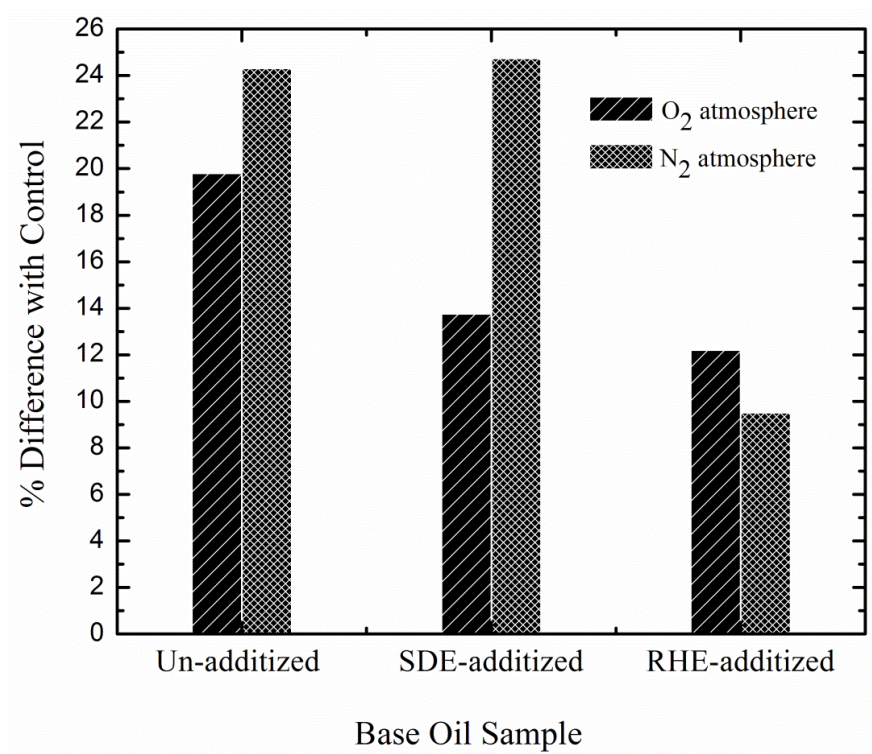


Fig.3.64. Comparison of percent differences of T_{onset} of the un-additized, RHE- and SDE-additized base oil samples oxidized at 200 °C with control sample

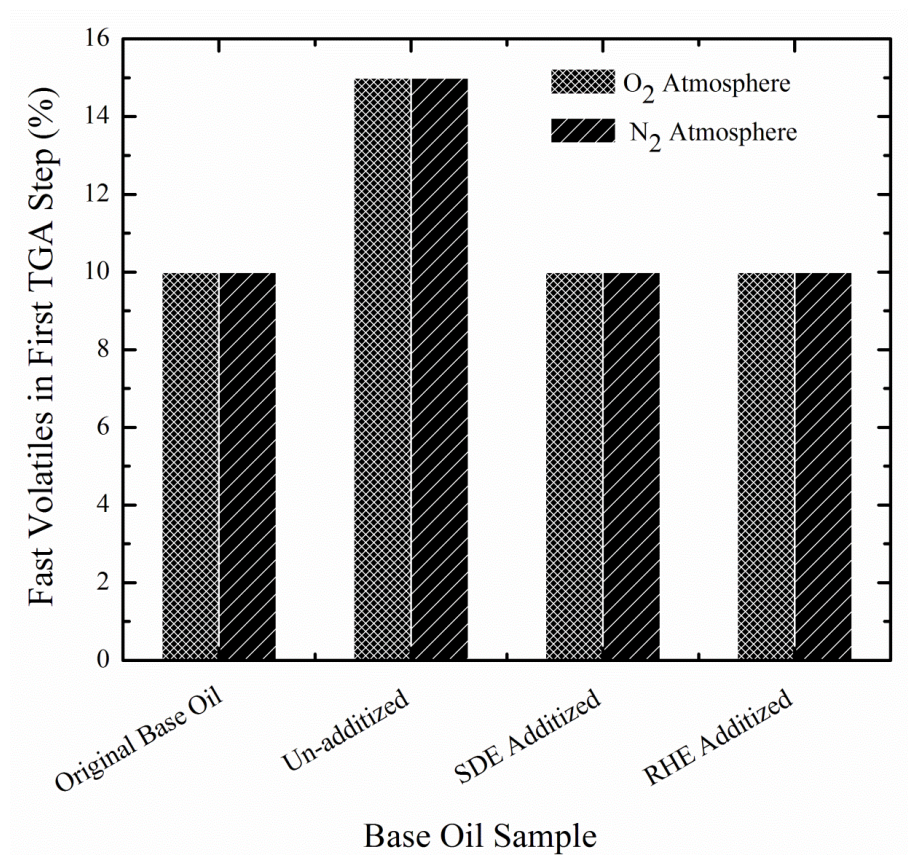


Fig.3.65. Comparison of fast volatiles evolved during first degradation step of the un-additized, RHE-and SDE-additized base oil samples oxidized at 200 °C with control sample

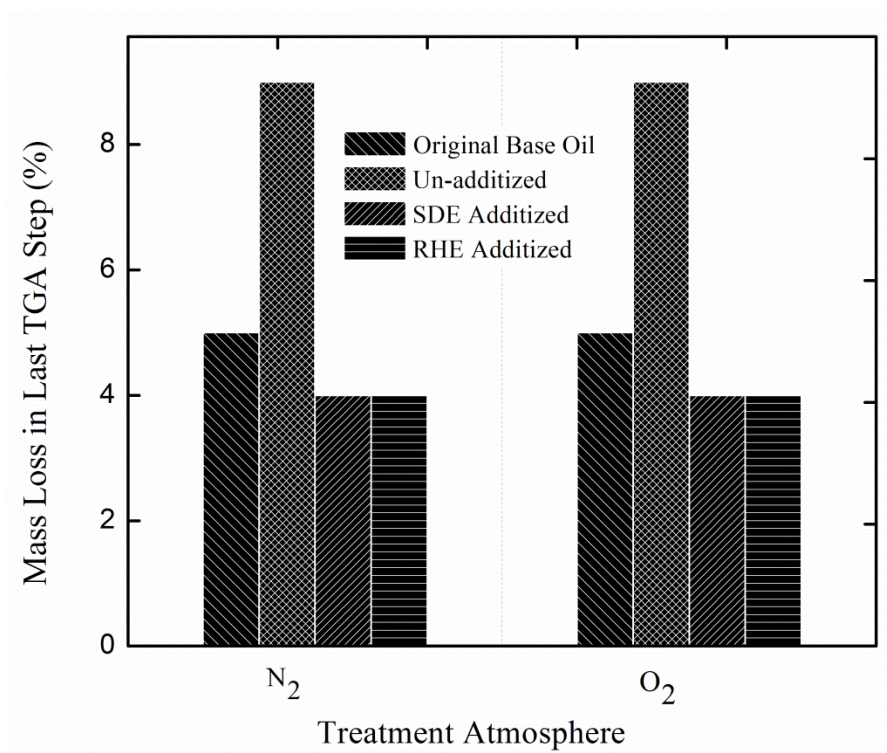


Fig.3.66. Comparison of weight gain of the un-additized, RHE- and the SDE-additized base oil samples oxidized at 200 °C with control sample



PHASE-VI

Next to TGA, calorimetric analyses in terms of oxidation induction time(OIT) in case of the oil samples spiked with bio mass derived extracts in comparison with the un-additized MBO samples were performed and discussed.

3.6. DIFFERENTIAL SCANNING CALORIMETRIC ANALYSIS

Differential Scanning Calorimetry (DSC) is one of the most frequently used techniques generally employed to measure the oxidation induction time (OIT) for investigating thermo-oxidative stability of many materials such as oil, fats, lubricant and pharmaceuticals. The calorimeter measures the heat flow in and out of the sample in the form of endothermic or exothermic peaks in the PDSC profile [79]. In the oil analysis, particularly PDSC employed for investigating oil stability in terms of onset decomposition temperature, and oxidative stability index (OSI time or OSI temperature) [80,81]. Thermo-oxidative stability of oil is assessed by subjecting the oil sample either to a programmed temperature (range of temperatures) or constant temperature in the presence of pressurized O₂. In programmed temperature analyses, range of temperature is plotted against the heat flow at a specific rate i.e. 10°C/min which gives the onset decomposition temperature of oil. In constant temperature or isothermal analysis, the sample is oxidized in pressurized O₂ purge kept at constant temperature and time is taken versus the heat flow in the PDSC profile that give oxidation induction time (OIT). Programmed temperature analysis implies the oxidative and thermal stability of the oil as it is exposed to elevated temperature and air flow in engine and industrial machinery. For the non-isothermal studies, the temperature range used 50-350°C and the heating rate employed ranged from 1 to 25°C/min. The onset oxidation temperatures usually depend on the heating rate and composition of the oil sample.

Isothermal analysis determined the specific time of the oil to which it remain stable (undecomposed or un-oxidized) as it applied at a constant temperature for longer durations in the industrial and engine applications. The wide variety of different applications reflects the versatility of the PDSC technique for over 50 years. Usually there is a big difference found in the OIT value between Rancimat method and PDSC



isothermal method. This difference is because of the fact that small sample is used in PDSC experiments, allowing a higher oil-oxygen ratio in comparison with the Rancimat method. Moreover, to oxidize the oil, PDSC used pure oxygen (99% purity) while the Rancimat method employed air (~21% of oxygen). The onset heat flow signals the PDSC thermogram [82].

Oxidation induction time (OIT) is the time at which the exothermic peak appears due to decomposition of the oil in PDSC profile when the oil is oxidized at a particular constant temperature. The DSC cell temperature is kept at a specific isothermal temperature of interest to measure the OIT for oil or biomass extract. A dramatic increase for the evolved heat is detected by observing the sharp exothermic peak occurred due to oxidation reaction. The OIT is determined by extrapolating downward the PDSC peak of oxidation to the time axis. Oxidation induction times express the potential of engine oil to with stand against oxidation. OIT is influence by the nature of the antioxidants. After exhaustion of the antioxidant, the hydrocarbon chains are further oxidized by a radical mechanism which can be observed through an exothermic effect in the PDSC signal. It indicates that during induction period, the antioxidant resist oxidation which led to inhibition of oil degradation or otherwise [83].

Isothermal oxidation of oil used to assess the onset time which rank the oxidized oil in terms of their oxidative stability [84]. PDSC isothermal is more useful than OSI method because it consumes less time and less amount of sample [85]. Therefore, the OIT was determined at isothermal conditions of 100 °C and 200 °C. Original (un-oxidized), and un-additized, RHE- & SDE-additized base oils oxidized at 100 and 200 °C for 6 h were studied.

3.6.1. Isothermal Analysis of the Original and Various Oxidized Base Oil Samples (Un-Additized, RHE-& SDE- Additized)

3.6.1.1. Isothermal Analysis of Original Base Oil

Isothermal (100 °C) OIT Analysis

The isothermal (100 °C) OIT analysis of the original base oil (un-oxidized) was studied. The OIT value was found to be 52 min as displayed in PDSC thermograms given

in Fig.3.67 and Fig.3.69. The corresponding data is compiled in Table.3.14. The OIT value is found to be high which indicates the thermo-oxidative stability of the base oil under study.

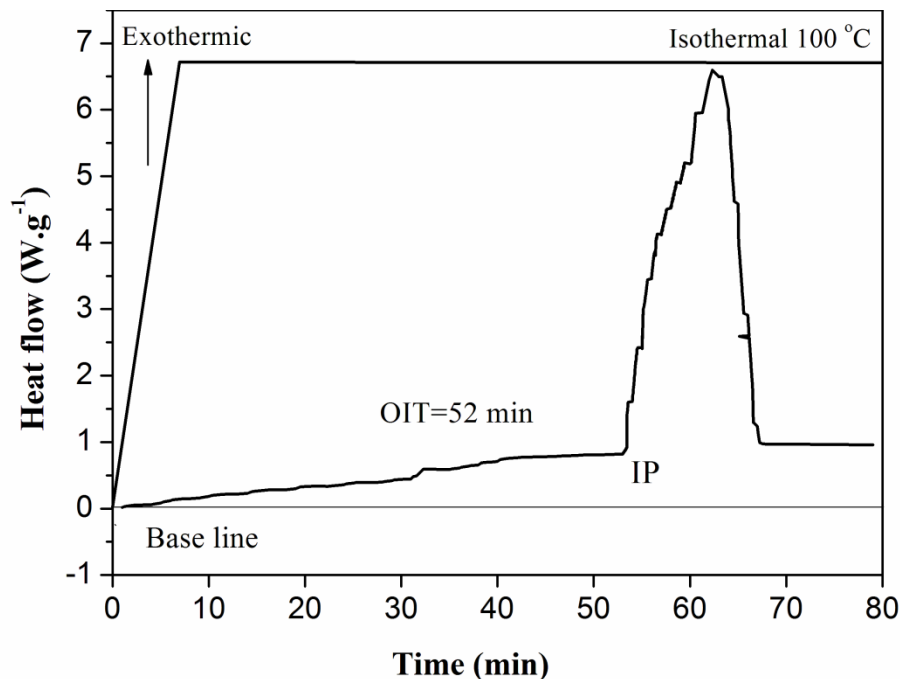


Fig. 3.67. Isothermal (100 °C) PDSC thermogram of the original (un-oxidized) base oil

Isothermal (200°C) OIT Analysis

The OIT analysis was performed in case of the original base oil at isothermal condition of 200°C. The PDSC thermogram is provided in Fig. 3.68. The OIT value determined was found to be 29.20 min as per data given in Table.3.14 and Fig.3.69.

Percent difference calculated between OIT values obtained at 100 and 200°C was calculated to be 80.31 %. The results clearly indicate the effect of temperature rise on the oxidative degradation of the base oil which shows a non linear inter-relationship.

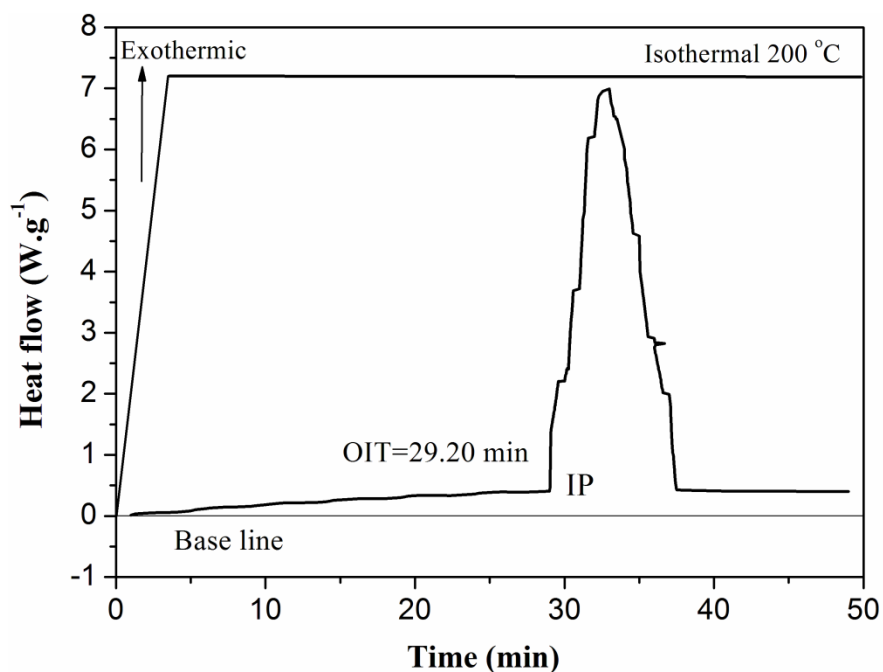


Fig.3.68. Isothermal (200°C) PDSC thermogram of the original (un-oxidized) base oil

Table.3.14. Isothermal (100 °C) and isothermal (200 °C) PDSC OIT Values of Original Base Oil

Sample	Isothermal Temperature(°C)	OIT (min)
Original base oil	100	52.0
	200	29.20



3.6.1.2. Isothermal Analysis of the Various Oxidized Base Oil Samples

OIT Analysis of Various Base Oil Samples Oxidized at 100 °C for 06 Hours

Isothermal (100 °C) OIT Analysis

The OIT was determined at isothermal conditions of 100 °C for the base oil samples oxidized at 100 °C for 6h i.e. un-additized, RHE-and SDE-additized MBO samples. The results have been compiled in Fig. 3.69 (a), Fig. 3.69 (b) and Fig. 3.69 (c) and Table. 3.15.

At isothermal 100 °C, OIT determined in case of the un-additized base oil oxidized at 100 °C was found to be 42.40 min while in case of the RHE-and SDE-additized base oil samples, the OIT values were found to be 50.41 and 49.10 min, respectively.

The percent differences were calculated in case of the un-additized and additized MBO samples in comparison with the original MBO in order to investigate the thermo-oxidative stabilities particularly those of the additized samples. The results are graphically represented in Fig.3.71. The percent difference calculated between the original and the un-additized MBO was found to be 22.64 %. Similarly, in case of RHE- and SDE-additized MBO samples, the differences were found to be 3.15 % and 5.90 %, respectively. The results indicate a much larger reduction obtained in case of the additized samples when compared with the original oil. The data indicate that the percent difference of the RHE-additized sample with the original base oil was insignificant (3.15%) and in case of the SDE-additized was just significant (5.90%). The results inferred the outstanding antioxidant behavior of the RHE- and SDE-additized samples at isothermal condition of 100 °C.

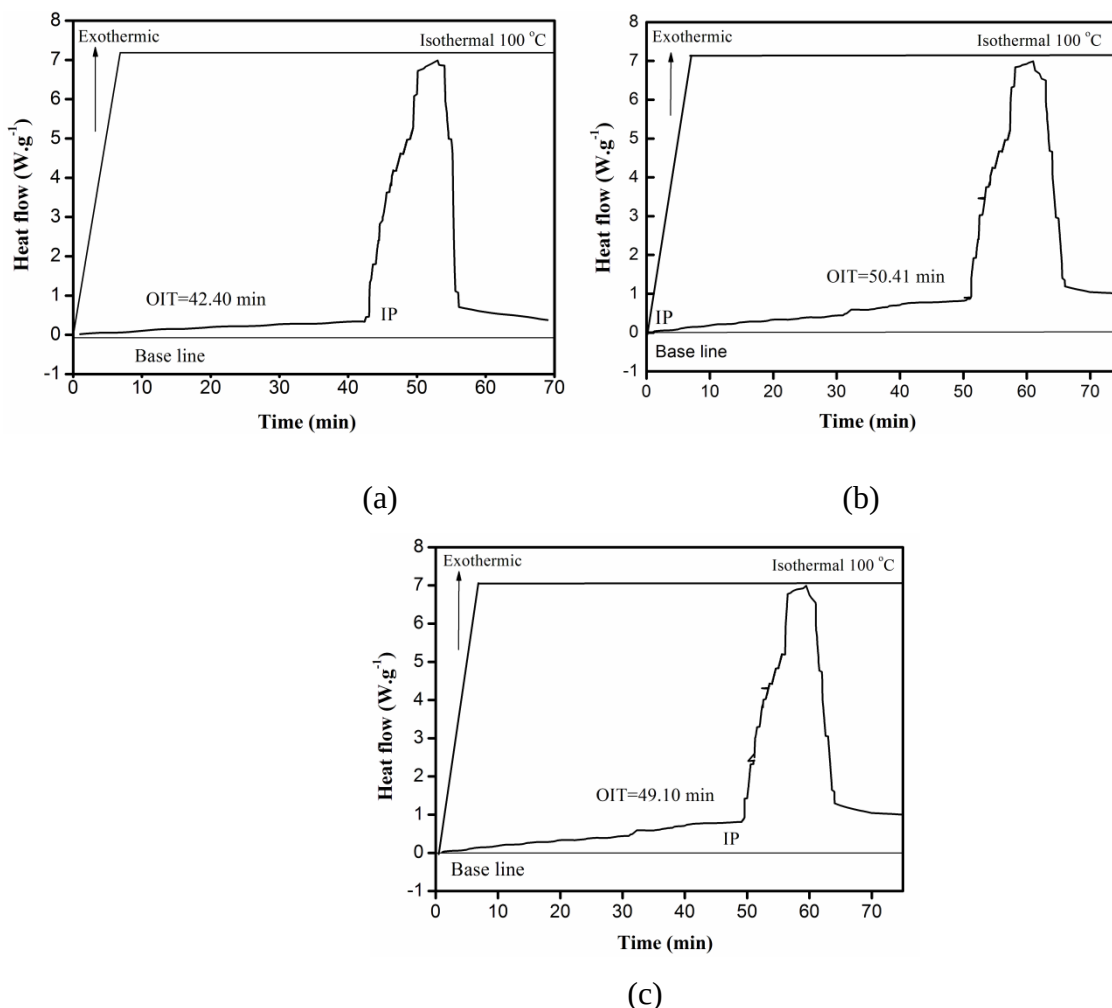


Fig.3.69. Isothermal (100°C) PDSC thermograms of the various base oil samples oxidized at 100°C , A: un-additized, B: RHE-additized and C: SDE-additized

Isothermal (200°C) OIT Analysis

The isothermal (200°C) OIT analysis of the various base oil samples oxidized at 100°C for 06 was also performed. The PDSC thermograms are provided in Fig.3.70 and the corresponding data is compiled in Table 3.15.

The OIT value found in case of the un-additized sample oxidized at 100°C was found to be 19.52 min. Under the same isothermal conditions, OIT value determined in case of the RHE- and SDE-additized MBO samples were found to be 28.11 and 27.10 min, respectively.

The percent difference in case of the un-additized, the RHE-and SDE-additized MBO samples were calculated with respect to original MBO. The percent difference in case of un-additized sample was found to be 48.56 %. While in case of additized samples of RHE and SDE, the percent differences were found to be 3.16 and 7.01 %, respectively as per data given in Fig.3.71. The results indicate a decline in the OIT values and also in percent differences in comparison with the original oil. The results suggest the outstanding antioxidant character of the RHE and SDE at isothermal condition of 200°C.

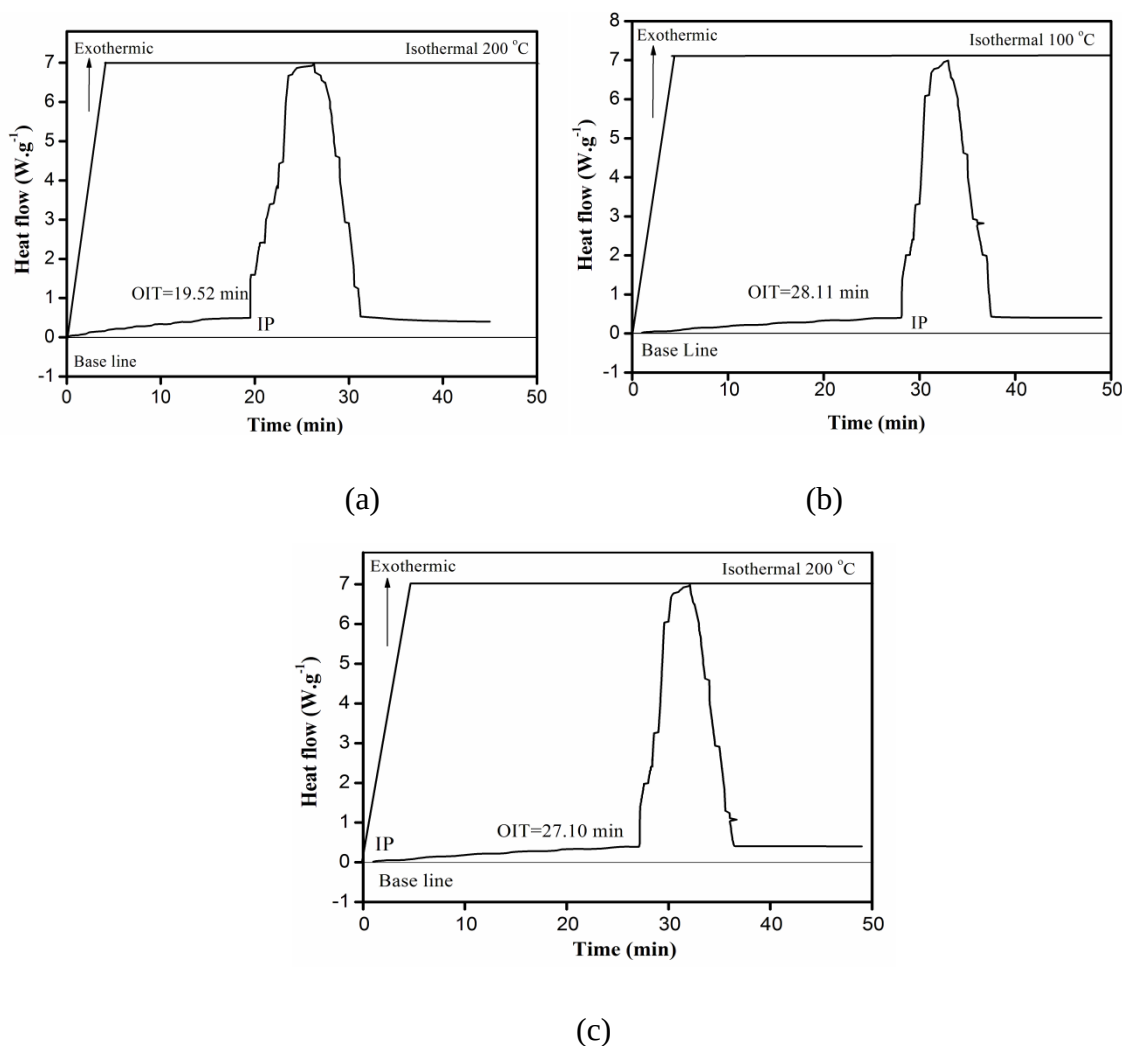


Fig.3.70. Isothermal (200 °C) PDSC thermograms of the various base oil samples oxidized at 100°C, A: un-additized, B: RHE-additized and C: SDE-additized



Table.3.15. PDSC OIT Values (isothermal 100 and 200 °C) of Un-additized, RHE- and the SDE-additized Base Oil Samples Oxidized at 100 °C for 06 Hours

Oil Sample	Oxidation Temperature (°C)	OIT (min)
Un-additized	100	42.40
RHE-additized	100	50.71
SDE-additized	100	49.10
Un-additized	200	19.52
RHE-additized	200	28.11
SDE –additized	200	27.10

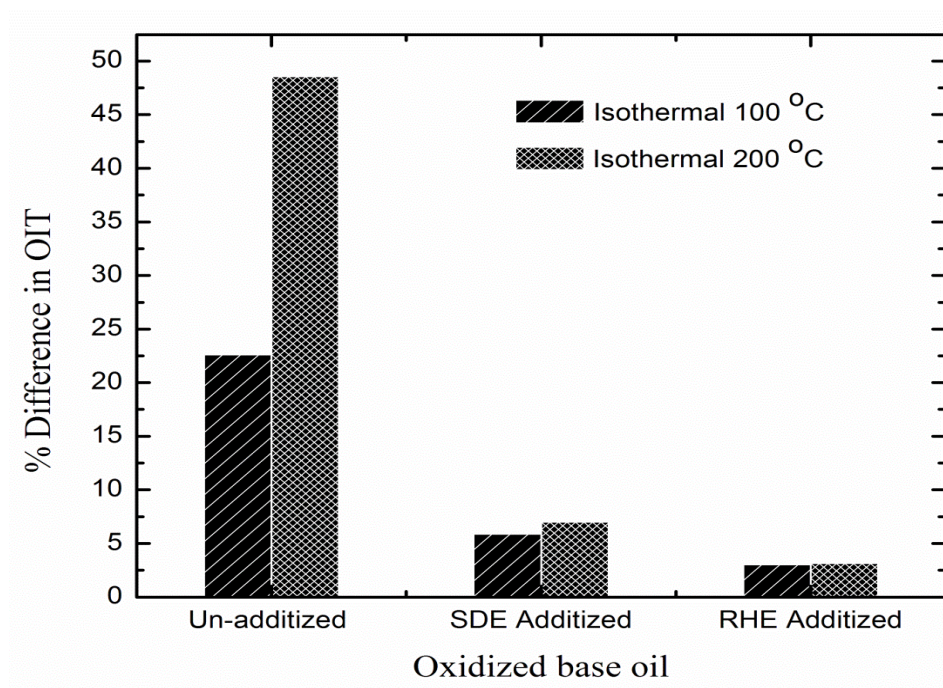


Fig. 3.71. Comparison of percent difference of un-additized, RHE- and SDE-additized base oil samples oxidized at 100 °C with the original base oil at isothermal 100 and 200 °C



3.6.1.3. Isothermal Analysis of the Various Oxidized Base Oil Samples

OIT Analysis of Various Base Oil Samples Oxidized at 200 °C for 06 Hours

Isothermal (100 °C) OIT Analysis

The OIT value decreased with the temperature rise and oxidation time as the oxidation or degradation rate is higher at elevated temperature. Less time is required for oxidation of hydrocarbons since low amount of molecules exist in un-decomposed form in an oil sample which is oxidized at elevated temperature. Moreover, the antioxidants resist oxidation to less period of time at elevated temperature as hydrocarbons get decomposed to greater extent [86].

The OIT values in case of the un-additized and additized MBO samples were determined and their percent difference with respect to the original oil were calculated. The results are given in Fig.3.72 and the corresponding data is compiled in Table 3.16. The OIT value determined in case of the un-additized base oil oxidized at 200 °C was found to be 31.20 min. The value is quite lower than obtained in case of the same oil oxidized oil at 100 °C (42.40 min).

The OIT value possessed the percent difference of about 66.67 % as compared with the original base oil. Likewise, OIT value determined in case of the RHE- and SDE-additized MBO samples oxidized at 200 °C were found to be 37.50 and 34.31 min bearing percent difference with the original base oil of 38.67 % and 51.55 % as clear from the displayed data (Fig. 3.72& Fig. 3.74 and Table.3.16). In this way, percent increase in OIT value achieved in case of the RHE-additized sample was observed to be 20.19 % and in case of the SDE-additized sample was 9.96 % with respect to the un-additized MBO which indicate their effective antioxidant behavior. From all of the results, one can evaluate the efficient antioxidant role of both of the RHE and SDE but not upto that extent as observed in case of oxidation performed at 100 °C.

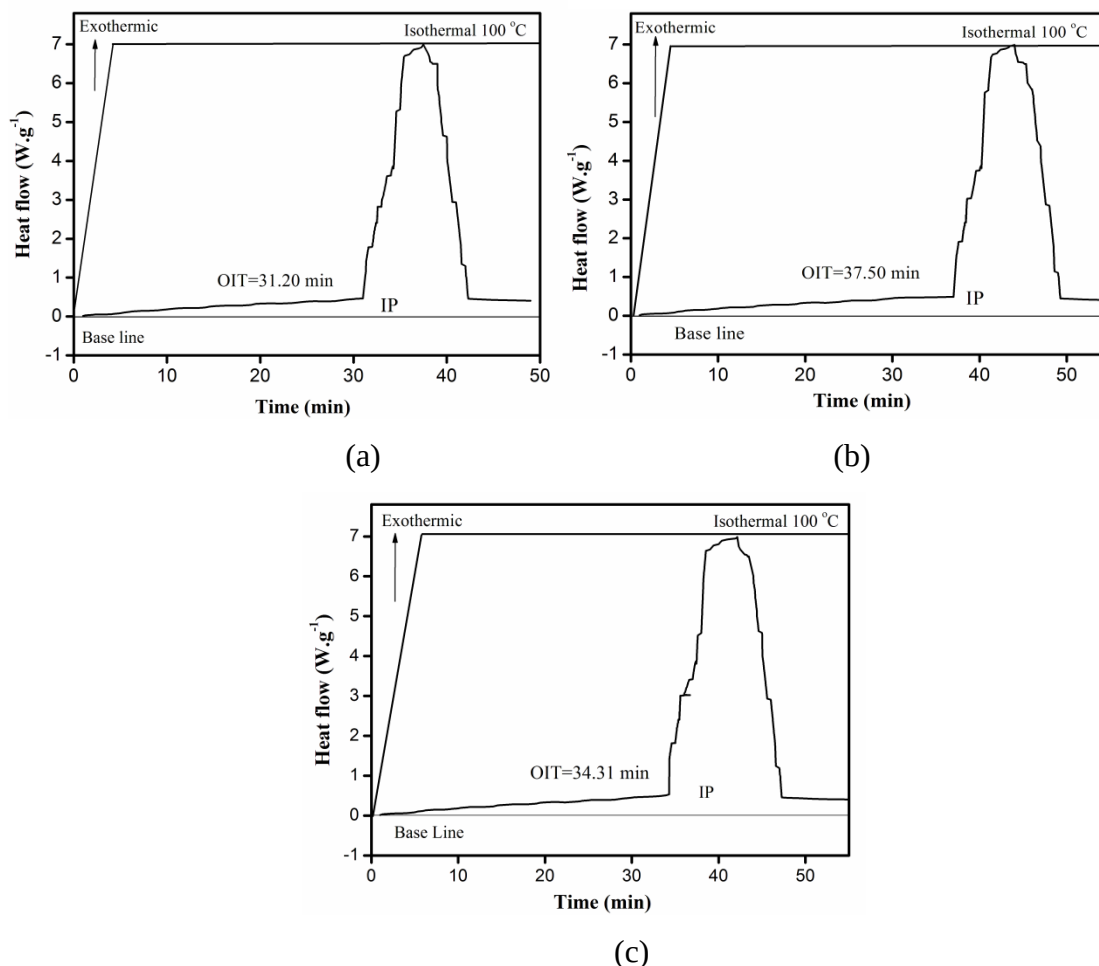


Fig.3.72. Isothermal (100 °C) PDSC thermograms of the various base oil samples oxidized at 200°C, A: un-additized, B: RHE-additized and C: SDE-additized

Isothermal (200 °C) OIT Analysis

The OIT Isothermal (200 °C) values determined in case of the base oil samples oxidized at 200 °C for 06 h are provided in Fig.3.73 and Table. 316. The results indicate that the OIT value of the un-additized, the RHE-and SDE-additized base oil samples were found to be 15.48, 20.57 and 19.39 min, respectively.

Percent differences in the OIT values were calculated in comparison with the original oil and found to be, 87.33, 40.90 and 49.56 %, respectively as per results provided in Fig.3.74.

From the results compiled one can conclude that both of the RHE and SDE worked very effectively in increasing the oxidative stability of the base oil by increasing the OIT values to a greater extent at both isothermal conditions of 100 and at 200 °C. However, the antioxidants role at isothermal 100 °C was more pronounced than at isothermal 200 °C in case of both of the RHE and SDE-additized samples. Base on the results, the RHE was found to be more efficient than the SDE at both isothermal conditions as antioxidant.

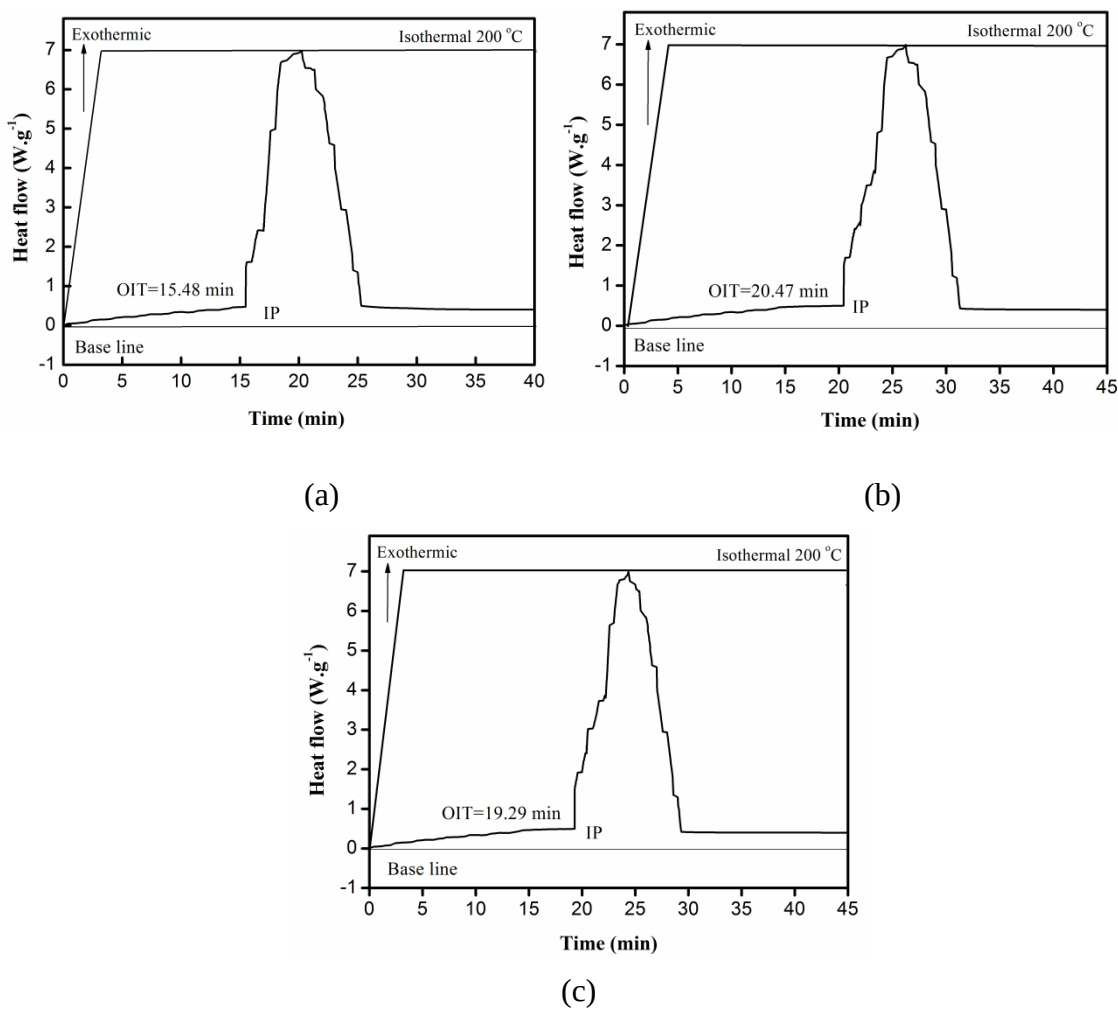


Fig.3.73. Isothermal (200 °C) PDSC thermograms of base oil samples oxidized at 200°C, A: un-additized, B: RHE-additized and C: SDE-additized



Table: 3.16. DSC OIT Values (isothermal 100 and 200 °C) of the Un-additized, RHE- and SDE-additized Base Oil Samples Oxidized at 200 °C for 06 Hours

Sample	Oxidation Temperature (°C)	OIT (min)
Un-additized oil	100	31.20
RHE-additized oil	100	37.50
SDE-additized oil	100	34.31
Un-additized oil	200	15.48
RHE-additized oil	200	20.47
SDE –additized oil	200	19.29

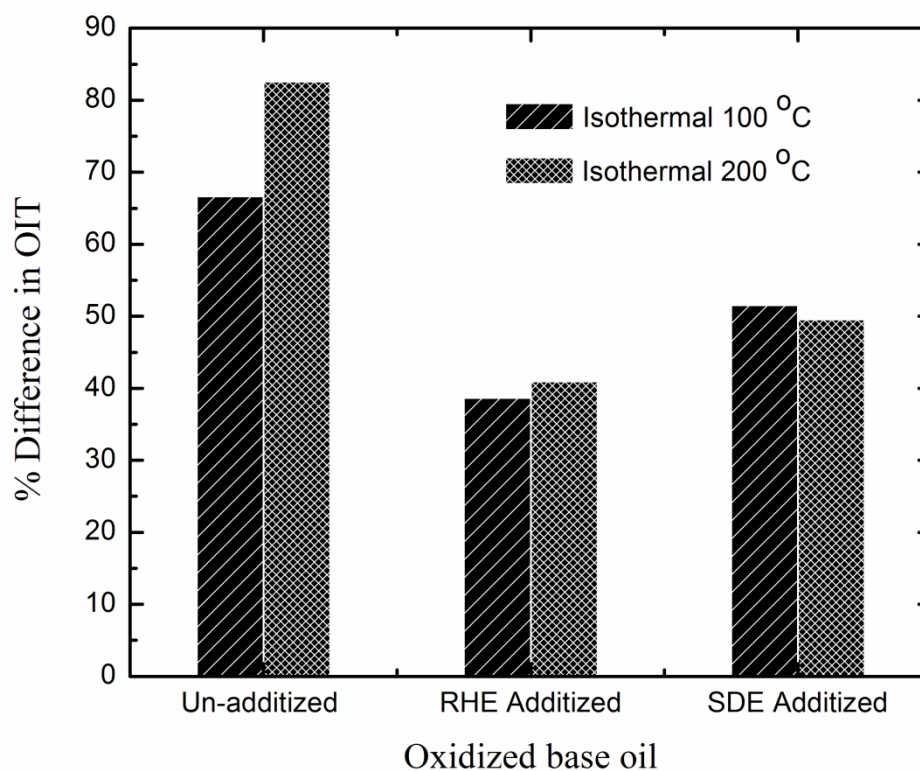


Fig.3.74. Comparison of percent difference of the un-additized, RHE-and SDE-additized base oil samples oxidized at 200 °C with the original base oil at isothermal 100 and 200 °C



PHASE-VII

In order to decide about changes in spectroscopic properties of the original and the variously oxidized residual oil samples, Gas chromatographic- Mass spectrometric analyses were carried out in order to ascertain the changes in the individual compounds, the hydrocarbon range products and the hydrocarbon group types. The results are presented in the proceeding section.

3.7. GC -MS ANALYSIS

The GC-MS analysis of the various samples was performed in order to investigate the antioxidant contents of the RHE and SDE under study as well as to study the compositional changes during oxidations performed at 100 and 200 °C for time duration of 6 h in comparison with the original un-oxidized sample.

3.7.1. GC -MS Analysis of the RHE, SDE, Original (un-oxidized), and the Various Oxidized Base Oil Samples

3.7.1.1. GC-MS Analysis of RHE and SDE

The GC-MS spectra of the RHE and SDE are provided in Fig.3.75 and Fig.3.76. The individual components identified along with their retention times and relative abundance data is compiled in Table 3.17. Different organic compounds belong to various classes were identified in case of both of the RHE and SDE.

The results indicate that among the oxygenates, alcohols found in case of the RHE were found to be propanol and pentanol and in case of the SDE were 2, 3 butanediol and 10,12-hexadecadienol. The aldehydes identified were 2-butenal and 4-methyl benzaldehyde in the RHE and in SDE were 2-methylpentanal, 2, 4-dimethyl benzaldehyde, chloro- benzaldehyde, 5-methyl-4-furancarboxyldehyde and 2-hydroxy-5-methylbenzaldehyde.

Among the ketones in the RHE found were the cyclohexanone, 3-hydroxy cyclohexanone, 2,3-dihydroxy cyclohexanone, 3-methoxy acetophenone, 1,2-dihydroxyethyl-3,4-dihydroxyfuran-2-one, naphthoquinone, dibenzylideneacetone and



2,4-dicholo-3,6-dihydroxy-1,4-benzoquinone while in the SDE were hydroxy acetone, 2-cyclopenten-1-one, 4-hydroxy-2- pentanone, 3-methyl-2-cyclopentenone, 3-methyl, 2,4-pentanedione, 2-cyclohexanone, 2-methyl-4-hydroxy1-1cyclohexanone, 4-methyl acetophenone, 5-(1-hydroxyethyl) 3,4-dihydrofuran-2-one, 1,2-dihydroxyethyl, 3,4-dihydroxyfuran-2-one and 1-4-naphthoquinone.

The carboxylic acid members recognized in the RHE were acetic acid, propanoic acid, o-hydroxybenzoic acid and octadecanoc acid and in the SDE were acetic acid, propanoic acid, 4-hydroxybenzoic acid, 4-methyl-2-hydroxybenzoic acid, 4-methoxy-2-hydroxybenzoic acid, 2-Propyl, 4-hydorxy benzoic acid, 4-ethoxy, 2,6-dihydroxy benzoic acid, 4-amino benzene sulfonic acid, 2-propyl, 4-hydorxy benzoic acid and octadecanoic acid.

The major phenolics identified were phenol, 4-methoxy, o-xylene, 4-methoxy styrene, o-aminophenol, o-nitrophenol, p-cresol, o-bromophenol, 4-ethyl phenol, 4-methyl-1,2-dihydroxybenzene, 3,4,5-trihydroxybenzene, 2,6-xylenol, 8-hydroxy quinoline, 1,1-naphthalene, 2,2-diol, 1-nitroso-2-naphthol, p-anisol, xylenol, benzene-azo-2-b-naphthol, 4-methyl, 7-hyroxy-coumarine, alpha tocopherol and 2-nitro-1-naphthol. Similarly, in the SDE major phenolics found were phenol, 4-methoxy phenol, 2-ethoxy phenol, 2-Methyl-4-methoxy phenol, 2-methoxy-4-vinyl phenol, 4-ethyl phenol, 2,5-dimethyl phenol, 2,6-dimethyl phenol, 4-ethyl-2-methylphenol, 1,4-dihydroxybenzene, 3,4,5-trihydroxybenzene, 6-methyl-1,4-dihydroxybenzene, 2-methoxy-1,4-dihydroxybenzene, 6-ethoxy-1,4-dihydroxybenzene, 6-methoxy xylenol, 8-hydroxy quinoline, 1,1-naphthalene, 2,2-diol, nitroso-2-naphthol, 4-methyl, 7-hyroxy-coumarine, alpha tocopherol, nitro-naphthol and benzene-azo-2-b-naphthol.

Some other compounds with functional groups in the RHE were found to be amyl acetae, methyl methacrylate (ester), 2-methoxy toluene, 4-ethoxy tolune, 2,4-dimethoxy toluene, 4-ethoxy, 2 methoxy toluene and 2-ethyl, 4-methoxy toluene (alkoxylated aromatics), o-phenylenediamine, m-phenylenediamine and benzoyl phenyl hydroxyl amine (aromatic mine), methyl phenyl acetamide (aromatic amide), n-hexane, n-heptane, eicosane and docosane (paraffins). Similarly, in the SDE some other compounds identified with other aromatic functional groups were found to be 3,4-dihydorxy



cyclohexane, 4-ethyl-1-hydroxycyclohexane, 2,4-dimethyl-1-hydroxycyclohexane, 1-methoxy-1,3-cyclohexadiene, (hydroxylated naphthenes), 2,4-dimethoxy-6-methyl benzene and 6-ethoxy-1,2 dimethylbenzene (alkoxylated aromatics), o-benzoyl phenyl hydroxyl amine, amino pyridine (aromatic amine) and methyl phenyl acetamide (aromatic amide). The results are in consonance with the earlier studies [87-130].

The concentrations of different classes of compounds were calculated as per results given in Tables 3.17 and 3.18 which showed that these compounds belong to various families and found to be 0.880 & 4.313 % (alkanes/naphthenes), 2.308 & 1.652 % (alcohols), 0.618 & 1.837 % (aldehydes), 4.844 & 17.850 % (ketones), 7.619 & 4.744 % (carboxylic acids), 7.761 & 4.744 % (esters), 67.050 & 61.310 % (phenols and their derivatives) and 8.919 & 6.086 (aromatic amines/amides) in case of the RHE and SDE, respectively, as per results given in Table.3.17 and Table.3.18. For compounds having functional groups other than aldehydes and ketones, the concentrations were found to be 14.33 and 14.50 % in case of the RHE and SDE, respectively. As evident from the data, phenols and their derivatives were found to be the most abundant ingredients found in both of the samples. The concentrations of various families of compounds identified in both RHE and SDE have been summarized in Table 3.19. The order of the various classes of compounds regarding concentration determined as per given in Table 3.19 in case of the RHE was:

Phenolics>aromatic amines>esters>carboxylic acids>ketones>alcohols >alkanes>aldehydes

Likewise, in case of the SDE, the order was found to be:

Phenolics>ketones>aromaticamide>carboxylicacids>naphthenes>esters>aldehyde
s>alcohols

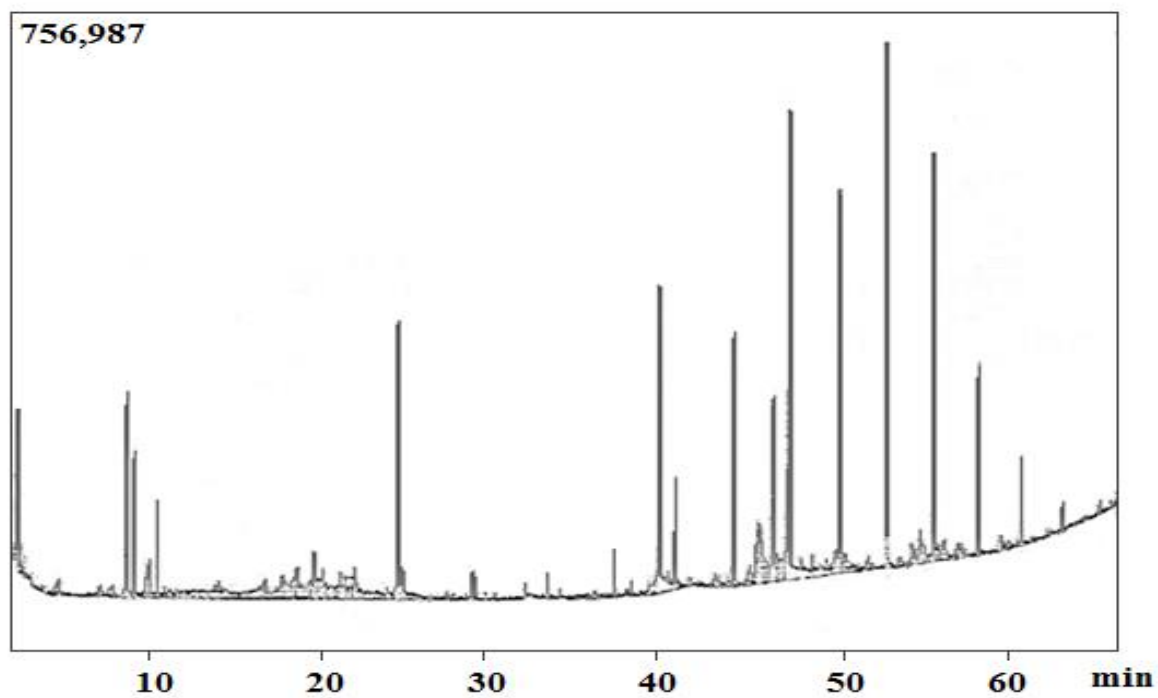


Fig.3.75. GC-MS chromatogram of original RHE

**Table.3.17. Individual Compounds Identified in RHE**

S.#	Compound	Molecular Formula	Molecular Mass	t _R (min)	Conc. (%)
1	Acetic acid	C ₂ H ₄ O ₂	60	1.856	1.210
2	Propanol	C ₃ H ₈ O	60	2.152	2.094
3	Propanoic acid	C ₃ H ₆ O ₂	74	2.634	4.721
4	Butanal	C ₄ H ₆ O	72	1.924	0.424
5	Pentanol	C ₅ H ₁₂ O	88	2.341	0.214
6	n-Hexane	C ₆ H ₁₄	86	2.651	0.205
7	n-Heptane	C ₇ H ₁₆	100	2.964	0.209
8	Methyl methacrylate	C ₅ H ₈ O ₂	100	10.132	4.326
9	Amyl acetate	C ₇ H ₁₄ O ₂	130	10.237	3.435
10	Cyclohexanone	C ₆ H ₁₀ O	98	11.254	0.392
11	3-Hydroxy cyclohexanone	C ₆ H ₁₀ O ₂	114	11.935	0.355
12	2,3-Dihydroxy cyclohexanone	C ₆ H ₁₀ O ₂	130	12.452	1.858
13	2-Methoxy toluene	C ₈ H ₁₀ O	122	13.245	0.921
14	2-Methyl acetophenone	C ₉ H ₁₀ O	134	16.756	0.562
15	4-Methyl benzaldehyde	C ₈ H ₈ O	120	16.065	0.194
16	3-Methoxy acetophenone	C ₉ H ₁₀ O ₂	150	18.316	0.231
17	4-Ethoxy toluene	C ₉ H ₁₂ O	136	19.820	0.118
18	2,4-Dimethoxy toluene	C ₉ H ₁₂ O ₂	152	22.299	0.816
19	4-Ethoxy, 2 methoxy toluene	C ₁₀ H ₁₄ O ₂	166	24.542	0.243
20	2-Ethyl, 4-methoxy toluene	C ₁₀ H ₁₂ O	151	25.421	0.118
21	Phenol	C ₆ H ₆ O	94	26.423	5.180
22	4-Methoxy, o-xylene	C ₉ H ₁₂ O	136	32.674	0.446
23	4-Methoxy styrene	C ₉ H ₁₀ O	134	36.851	0.212
24	1,2-Dihydroxyethyl,3,4-dihydroxyfuran-2-one	C ₆ H ₈ O ₆	176	39.327	0.408
25	O-Aminophenol	C ₆ H ₇ NO	109	42.329	5.798
26	O-Nitrophenol	C ₆ H ₅ NO ₃	139	43.757	3.007
27	p- Cresol	C ₇ H ₈ NO	108	46.862	5.635
28	O-Bromophenol	C ₆ H ₅ BrO	173	47.321	0.865
29	4-Ethyl phenol	C ₈ H ₁₀ NO	122	47.986	0.934
30	4-Methoxy-phenol	C ₇ H ₈ O ₂	124	49.521	3.910
31	4-Methyl 1,2-dihydroxybenzene	C ₇ H ₈ NO ₂	124	49.824	9.787
32	3,4,5-Trihydroxybenzene	C ₆ H ₆ O ₃	126	52.914	11.733



33	Benzoyl phenyl hydroxyl amine	$C_{13}H_{11}NO_2$	213	55.873	8.585
34	O-Phenylendiamine	$C_6H_8N_2$	108	56.425	0.221
35	m-Phenylendiamine	$C_6H_8N_2$	108	57.342	0.113
36	2,6-Xylenol	$C_8H_{10}O$		57.938	0.731
37	o-hydroxybenzoic acid	$C_7H_6O_3$	138	58.231	0.784
38	8-Hydroxy quinoline	C_9H_7NO	145	58.526	0.325
39	1,1-Naphthalene, 2,2-diol-	$C_{10}H_8O_2$	160	58.192	8.783
40	1-Nitroso-2-naphthol	$C_{10}H_7NO_2$	173	59.057	0.323
41	Naphthoquinone	$C_{10}H_6O_2$	158	59.428	0.306
42	2,4-Dicholo, 3,6-dihydroxy-1,4-benzoquinone	$C_6H_2Cl_2O_4$	208	59.731	0.372
43	Dibenzylideneacetone	$C_{17}H_{14}O$	234	59.962	0.361
45	4-Methyl, 7-hydroxy-coumarine	$C_{10}H_8O_3$	176	61.351	4.847
46	Alpha tocopherol	$C_{29}H_{50}O_2$	430	64.433	2.318
47	2-Nitro-1-naphthol	$C_{10}H_7NO_3$	189	66.321	00
48	Octadecanoic acid	$C_{18}H_{36}O_2$	284	68.124	0.904
49	Eicosane	$C_{20}H_{42}$	282	69.134	0.212
50	Docosane	$C_{22}H_{46}$	310	69.481	0.254

As reported by many researchers, phenols, their derivatives and aromatic amines were found to be the most effective antioxidants that exist in the RHE and SDE [131-143]. Among these phenolics, aromatic amines, tocopherols, stearic acid, ascorbic acid and citric acid are the most fruitful [131]. All of these are reported to be radical scavengers except the citric acid which act as chelating agent [132]. These antioxidants are extensively used in lubricants to enhance their thermo-oxidative stability individually. Engine oil increasingly use phenolic, aminic and organometallic antioxidants by trapping peroxy radicals or decomposing peroxides thereby acting as synergist with amine (both antioxidant and antiwear). Moreover, aromatic amines and polyphenols (having two aromatic rings) are more effective than simple phenolic antioxidant. It is because of the fact that each phenol molecule scavenged two peroxy radicals and each amine and polyphenol trapped four peroxy radicals [133]. Phenolics antioxidants are the first class of antioxidants discovered possessing extensive applications in food stuffs and in engine oil [134]. Phenolic antioxidants are mostly employed in situation where temperature



doesn't exceed 180⁰C [135] while amines are used at temperature zone above 200⁰C [136].

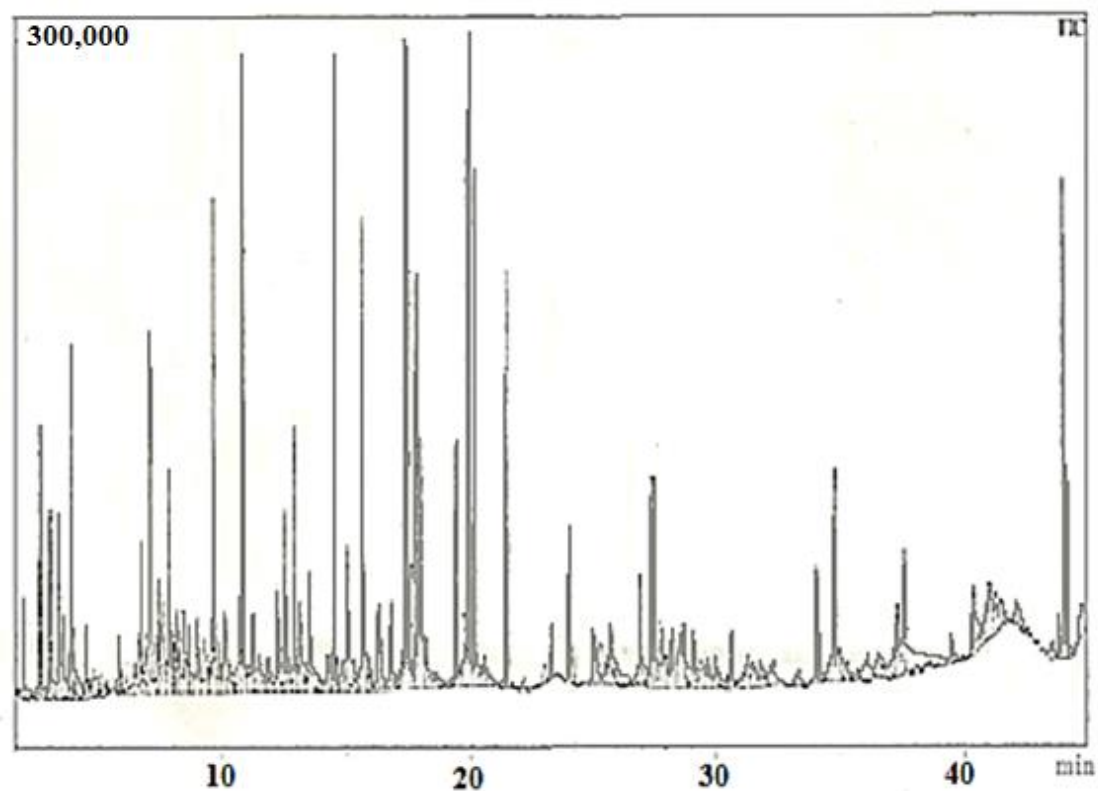


Fig.3.76. GC-MS chromatogram of original SDE



Table.3.18. Individual Compounds Identified in SDE

S.#	Compound	Molecular Formula	Molecular Mass	t _R (min)	Conc. (%)
1	Acetic acid	C ₂ H ₄ O ₂	60	0.492	1.022
2	Hydroxy acetone	C ₃ H ₆ O ₂	74	1.213	2.311
3	Propanoic acid	C ₃ H ₆ O ₂	74	2.137	1.323
4	2,3-Butanediol	C ₄ H ₁₀ O ₂	90	2.424	1.343
5	n-Hexane	C ₆ H ₁₄	86	2.611	0.752
6	2-Cyclopenten-1-one	C ₅ H ₆ O	82	2.741	1.554
7	2-Methylpentanal	C ₆ H ₁₂ O	100	2.851	0.502
8	Methyl methacrylate	C ₅ H ₈ O ₂	100	2.987	2.208
9	3-Methyl-2-cyclopentennone	C ₆ H ₈ O	96	3.204	1.336
10	3-Methyl, 2,4-pentanedione	C ₆ H ₁₀ O ₂	114	4..337	0.386
11	2-Cyclohexanone	C ₆ H ₁₀ O	98	5.711	2.592
12	3,4-dihydorxy cylcohexane	C ₆ H ₁₀ O ₂	114	6.135	0.755
13	2-Methyl-4-hydroxy1-1cyclohexanone	C ₇ H ₁₂ O ₂	128	6.325	0.721
14	4-Ethyl-1-hydroxycyclohexane	C ₈ H ₁₆ O	128	7.152	1.851
15	2,4-Dimethyl-1-hydroxycylcohexane	C ₈ H ₁₆ O	128	7.456	0.667
16	4-Methyl acetophenone	C ₉ H ₁₀ O	134	7.345	0.821
17	2,4-Dimethyl benzaldehyde	C ₉ H ₁₀ O	134	8.565	0.643
18	5-Methyl-4-furancarboxyldehyde	C ₉ H ₁₀ O ₂	150	8.916	0.692
19	5-(1-Hydroxyethyl) 3,4-dihydrofuran-2-one	C ₆ H ₁₀ O ₃	130	9.623	3.873
20	1-Methoxy-1,3-cyclohexadiene	C ₇ H ₁₀ O	110	10.106	0.288
21	2,4-Dimethoxy-6-methyl benzene	C ₉ H ₁₂ O ₂	152	10.259	0.275
22	6-Ethoxy-1,2 dimethylbenzene	C ₁₀ H ₁₄ O	150	10.345	0.138
23	2-Ehyl, 4-methoxy toluene	C ₁₀ H ₁₂ O	148	10.421	0.626
24	Phenol	C ₆ H ₆ O	94	10.826-	5.780
25	4-Methoxy phenol	C ₇ H ₈ O ₂	124	11.274	0.702
26	2-Ethoxy phenol	C ₈ H ₁₀ O ₂	138	12.351	0.991
27	1,2-Dihydroxyethyl, 3,4-	C ₆ H ₈ O ₆	176	12.528	1.547



	dihydroxyfuran-2-one				
28	O-Aminophenol	C_6H_7NO	109	12.829	2.385
29	2-Hydroxy-5-methylbenzaldehyde	$C_7H_8O_2$	136	12.957	0.807
30	2-Methyl-4-methoxy phenol	$C_8H_{10}O_2$	138	13.362	1.192
31	2-Methoxy-4-vinyl phenol	$C_9H_{10}O_2$	150	14.321	5.254
32	4-Ethyl phenol	$C_8H_{10}O$	122	15.286	1.288
33	2,5-Dimethyl phenol	$C_8H_{10}O$	122	15.421	4.210
34	2,6-Dimethyl phenol	$C_8H_{10}O$	122	16.224	0.789
35	4-Ethyl-2-methylphenol	$C_9H_{12}O$	136	16.717	0.837
36	1,4-Dihydroxybenzene	$C_6H_6O_2$	110	17.685	5.865
37	3,4,5-Trihydroxybenzene	$C_6H_6O_3$	126	17.965	3.714
38	6-Methyl-1,4-dihydroxybenzene	$C_7H_8O_2$	124	18.022	2.382
39	2-Methoxy-1,4-dihydroxybenzene	$C_7H_8O_3$	140	19.524	2.295
40	Benzoyl phenyl hydroxyl amine	$C_{13}H_{11}O_2N$	213	19.873	5.785
41	6-Ethoxy-1,4-dihydroxybenzene	$C_8H_{10}O_3$	154	20.231	4.421
42	2,4 -Diaminophenol	$C_6H_8ON_2$	124	21.435	3.728
43	2,6-Diaminophenol	$C_6H_8ON_2$	124	23.341	0.513
44	6-Methoxy xylenol	$C_{12}H_9O_2$	152	25.241	1.551
45	4-hydroxybenzoic acid	$C_7H_6O_3$	138	25.231	0.424
46	4-Methyl-2-hydroxybenzoic acid	$C_8H_8O_3$	152	25.314	0.314
47	4-Methoxy-2-hydroxybenzoic acid	$C_8H_8O_4$	168	25.712	0.415
48	1,4-Dihydroxy, 2,6-xylene	$C_8H_{10}O_2$	138	26.123	0.804
49	8-Hydroxy quinoline	C_9H_7ON	145	27.526	1.725
50	methyl phenyl acetamide	$C_9H_{11}ON$	149	27.753	0.382
51	amino pyridine	$C_5H_6N_2$	94	28.264	0.301
52	2-Propyl, 4-hydroxy benzoic acid	$C_{10}H_{12}O_3$	180	28.831	0.285
53	4-Ethoxy, 2,6-dihydroxy benzoic acid	$C_9H_{10}O_5$	198	29.248	0.393
54	4-Amino benzene sulfonic acid	$C_6H_7O_3NS$	173	30.624	0.321
55	1,1-Naphthalene, 2,2-diol-	$C_{10}H_8O_2$	160	34.192	1.134
56	Nitroso-2-naphthol	$C_{10}H_7NO_2$	173	34.957	1.898
57	1-4-Naphthoquinone	$C_{10}H_6O_2$	158	37.328	0.501
58	4-Methyl, 7-hydroxy-coumarine	$C_{10}H_8O_3$	176	37.531	0.872
59	Alpha tocopherol	$C_{29}H_{50}O_2$	430	39.562	1.124
60	Nitro-naphthol	$C_{10}H_7NO_3$	189	40.423	0.786
61	10,12-Hexadecadienol	$C_{16}H_{28}O$	236	40.843	0.309
62	Octadecanoic acid	$C_{18}H_{36}O_2$	284	41.241	0.247
63	2,4-Dimethyl anthracene	$C_{16}H_{14}$	206	41.658	0.124
64	Eicosane	$C_{20}H_{42}$	282	41.825	0.128



The antioxidants found in the biomass under study that is in the RHE and SDE used in avoiding thermo-oxidative deterioration of oil were dihydroxy benzene, pyrogallol, alkylated phenols (anisols) and aromatic amines, hydro-quinone, naphtho-quinone, hydroxy benzoic acid, hydroxy quinoline, carboxylated furanone, hydroxy benzaldehyde, alkylated hydroxyl coumarine, naphthol, aromatic amines or amides, ascorbic acid, stearic acid, tocopherols etc. [129-143]. All of the aforementioned antioxidants i.e. phenolics, aromatic amines and their derivatives have been used on commercial scale in blended form with lubricant from several decades in individual forms.

Table: 3.19. Summary of Various Classes of Compounds Identified in RHE and SDE

Conc. of various classes of compounds (%)	Methanolic Extract	
	RH	SD
Alkanes/ Naphthenes	0.880	4.313
Alcohols	2.308	1.652
Aldehydes	0.618	1.837
Ketones	4.844	17.850
Carboxylic acids	7.619	4.744
Esters	7.761	2.208
Phenolics	67.050	61.310
Aromatic amines/amides	8.919	6.086

3.7.1.2. GC-MS Analysis of the Un-oxidized Original Base Oil

The chemical composition of the un-oxidized MBO was studied by GC-MS. The results are provided in Table 3.20. The corresponding GC-MS spectrum is given in Fig. 3.77.

The results indicate the presence of various classes of compounds including paraffins, olefins, naphthenes and aromatics as clear from the abundant small, medium



and large intensity peaks [144]. The paraffins identified were found to be n-heptane, 2,5-dimethyl- octane, 4-methyl- octane, nonane, 3-ethyl-2,4-dimethyl pentane, 2,6-dimethyl octane, nonane, 2-dimethyl nonane, 3-dimethyl decane, 2,3,6-trimethyl octane, undecane, 5-methyl undecane, dodecane, 6-methyl tridecane, tetradecane, pentadecane, 5-propyl decane, hexadecane, heptadecane, 3-methyl hexadecane, octadecane, 2,6,10,14-tetramethyl hexadecane, tetratriacontane, nonadecane, eicosane, octadecane, henicosane, docosane, octacosane, tetracosane, and hexacosane.

Among the olefins, the major compounds identified were found to be 2-methyl-1-hexene, 2, 3, 4-trimethyl 2-pentene, 2-nonene, 5-methyl- (Z) 2-decene, and Z, E-7, 11-hexadecadiene-1-yl acetate. The aromatics verified were; toluene, ethyl benzene, 1, 3-dimethyl benzene, 1-ethyl-3-methyl benzene, 1,2,4-trimethyl benzene, and 1-ethyl-2,3-dimethyl benzene while among the naphthenes identified were; cyclohexene, 1,1,3-trimethyl cyclohexane, propyl cyclohexane, 1-methyl, 3-propyl cyclohexane, and butyl cyclohexane, 2-methyl, 3-isopentyl cycloheptanone, and cyclododecane .

The GC-MS data was used to determine the distribution of the different hydrocarbons range compounds. The relative abundance of hydrocarbons types i.e. paraffins, olefins, naphthenes and aromatics were calculated. The results are provided in Table 3.20 and Fig. 3.81. The proportions of paraffins, olefins, naphthenes and aromatics were found to be 92.719, 2.389, 2.198 and 2.694 %, respectively. Based on the results, the original oil fractional hydrocarbons distribution followed the given order:

Paraffins>naphthenes>olefins>aromatics

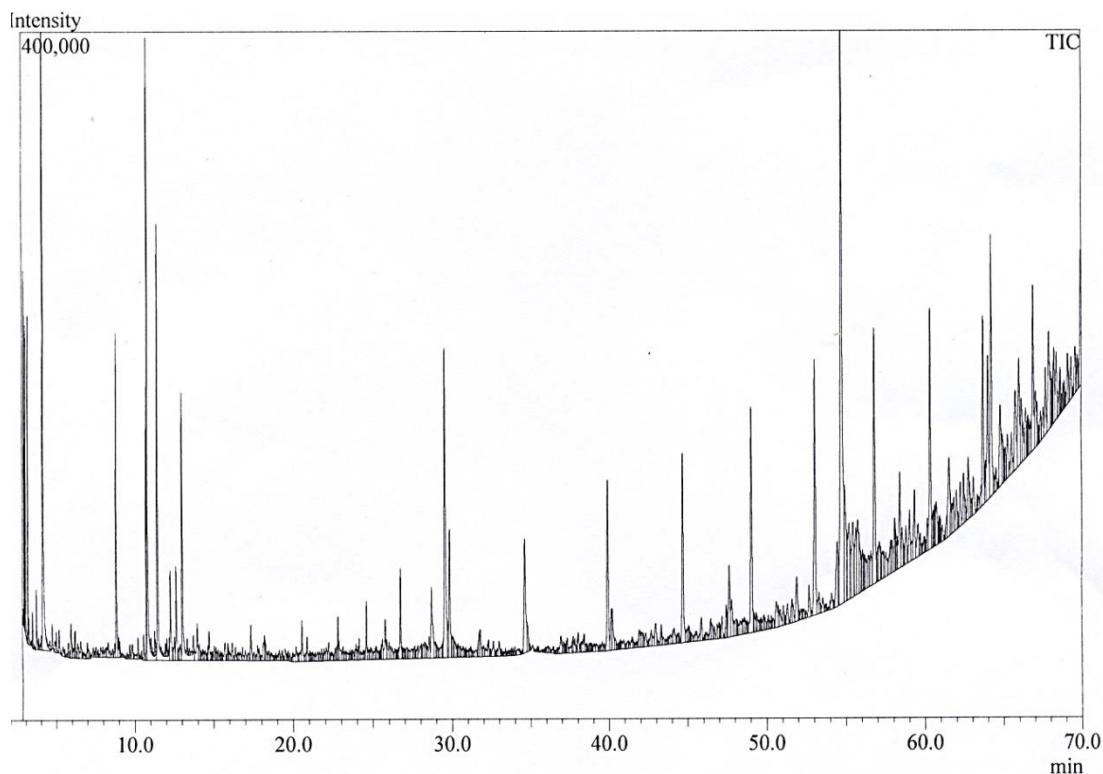


Fig.3.77. GC-MS chromatogram of original MBO

It is in general practice that the base oil which is used to formulate a good lubricant shall contains C_{18} - C_{35} range hydrocarbons having concentration $> 50\%$ [138]. The different carbon range hydrocarbons were found to be C_6 - C_{11} , C_{12} - C_{17} and C_{18} - C_{35} possessing concentration of 31.019, 15.440 and 53.541 % as per results provided in the Table. 3.21. It can be observed that the concentration of the heavy hydrocarbons ranges from C_{18} - C_{35} which lie within the range of a lubricant specification is significant than the hydrocarbons that fall in the fuel range such as gasoline (C_5 - C_{11}), kerosene (C_{12} - C_{15}) and diesel fuel oil (C_{16} - C_{18}). The fuel range hydrocarbons are usually blended with the heavier ones to produce good lubricity for a desired lubricant [145]. The various carbon number distribution hydrocarbons followed the order:

$$C_{18}-C_{35} > C_6-C_{11} > C_{12}-C_{17}$$



3.7.1.3. GC-MS Analysis of Various Base Oil Samples Oxidized at 100 °C for 06 Hours

The GC-MS analysis of the various base oil samples (the un-additized, the RHE- and the SDE additized) oxidized at 100 °C for 06 hours was also performed. The corresponding GC-MS spectra are provided in Fig. 3.78-Fig.3.80 and the related GC-MS data is given in Table- 3.20.

The chromatogram of the un-additized base oil oxidized at 100°C for 06 h showed some intense peaks (10-52 min) which indicate peaks characteristics for lube oil range hydrocarbons i.e. C₁₀-C₂₆ as shown in Fig.3.83. GC-MS data demonstrated that the un-additized base oil sample contains broad range of aliphatic and aromatic hydrocarbons as per results given in Table 3.19. There were some gasoline range aliphatic and aromatic compounds (C₆-C₉) identified (1-9 min) which is usually added to impart good lubricity to the lubricant.

The composition of the un-additized base oil after oxidation was found to be similar with the original base oil (un-oxidized) except in terms of aliphatic and aromatic hydrocarbons whose presence was confirmed by the appearance of some new peaks which may be due to the degraded compounds. The new compounds among the paraffins were found to be 3-methyl heptane, 3-ethyl-,2,7-dimethyl octane, 2-methyl-3-methylene nonane, 3,7-dimethyl nonane, 3,9-dimethyl undecane, 3-methyl tridecane, 4-methyl tridecane, tetradecane, 2,6,11-trimethyl dodecane, 2,6,10,15-tetramethyl heptadecane, 2-methyl heptadecane, 4-methyl pentadecane, hentriacontane, pentatriacontane, teracosane, pentacosane, hexacosane and octacosane.

Some new olefins identified were found to be 2,3-dimethyl 1-hexene, 4-nonene, 2-methyl 2-heptene, 3-hexadecene (Z), 7-tetradecene (Z) and 1-tetradecene. Among the aromatics, new compounds recognized were; 1-methyl-3-(1-methyl ethyl) benzene, 1,2,5-trimethyl benzene, 1,1-dimethyl propyl benzene, 2,6-dimethyl naphthalene and phenanthrene.

Two new naphthenes confirmed were cyclopentane -1-(2-methyl propyl) and 2-cyclohexyl undecane. While the carbonyl compound as oxidized degraded product found was 10-undecanoic acid, 3-methyl butyl ester.



Thus, the degraded composition contained the constituents like ester, alkylated benzene and alkylated PAHs (di and tricyclic), five and six membered alkylated naphthenes and some straight and branched olefins having carbon content of C_6 - C_{16} as new compounds. The results are in agreement with some earlier studies reported in the literature [139].

The hydrocarbon group type distribution of different compounds was also calculated from the GC-MS data which in turn employed to evaluate the degree of degradation. It is well established that the degree of degradation is assessed with the increase in concentration of naphthenes, olefins, aromatics or formation of new carbonyl compounds (aldehydes, ketones, carboxylic acids or esters). Ester is formed as a result of paraffins oxidation through the synthesis of alcohols, aldehydes/ketones and carboxylic acids as intermediate oxygenates [140]. The relative abundance of hydrocarbons types comprised of paraffins, olefins, naphthenes and aromatics was calculated from GC-MS analysis as compiled in Table 3.20. The proportions of the paraffins, olefins, aromatics, naphthenes and ester were found to be 87.892, 2.966, 5.448, 3.410 and 0.281 %, respectively as per results shown in Fig 3.81.

Thus, overall hydrocarbons of different carbon range identified were found to be C_6 - C_{11} , C_{12} - C_{17} and C_{18} - C_{35} . The concentration of the various carbon range hydrocarbons calculated were found to be 34.683 % (C_6 - C_{11}), 29.317 % (C_{12} - C_{17}) and 36.00 % (C_{18} - C_{35}), respectively as per results compiled in Table.3.21. It was investigated that the concentration of heavy hydrocarbons in the carbon range of C_{18} - C_{35} which fall in the lubricant range was lesser than obtained in case of the original base oil. The results reveal the degradation of heavy hydrocarbons. Moreover, the concentration of the hydrocarbons fall within the range of C_{18} - C_{35} comes out to be < 50 % signifies quality declination of the base oil under study. It shows that the base oil without antioxidant as additive is no longer useful as lubricant at 100 °C [145].

The formation of ester and the increase in the concentration of olefins, aromatics and naphthenes indicate significant level of degradation. The percent difference between the original base oil (un-oxidized) and the un-additized base oil oxidized at 100 °C in



terms of paraffin, olefin, aromatic and naphthenes contents calculated to be 4.827 %, 0.577 %, 3.250 %, 0.716 %, respectively as per results shown in Fig. 3.82.

Table.3.20. Individual Compounds Identified in the Original Un-oxidized and the Un-additized Base Oil Samples Oxidized at 100 °C

S. #	Compound	t _R	Conc. (%)	t _R	Conc. (%)
		Original Base Oil		Oxidized Base Oil	
Paraffins					
1	Heptane	2.964	2.045	3.154	2.565
2	Octane, 2,5-dimethyl-	4.883	0.186	4.870	1.317
3	*Heptane, 3-methyl-	---	---	5.136	0.602
4	Octane	6.190	0.729	6.178	1.555
5	Octane, 4-methyl-	8.706	0.248	8.691	0.678
6	*Octane, 3-ethyl, 2,7-dimethyl-	---	---	8.771	0.638
7	Nonane	10.181	0.358	10.167	1.090
8	Pentane, 3-ethyl-2,4-dimethyl-	10.794	14.952	10.789	5.227
9	Octane, 2,6-dimethyl-	11.436	3.831	11.440	4.185
10	Nonane, 2-methyl-	12.501	0.264	12.494	1.378
11	Nonane, 3-methyl-	12.862	0.130	12.857	0.731
12	Decane	13.631	0.582	13.924	2.410
13	Octane, 2,3,6-trimethyl-	14.684	0.424	14.678	1.930
14	Heptane, 2,5,5-trimethyl-	15.991	0.074	15.985	0.508
15	*Nonane, 3,7-dimethyl-	---	---	16.334	0.540
16	Undecane	17.321	0.649	17.315	2.281
17	Undecane, 5-methyl-	19.450	0.062	19.457	0.658
18	Dodecane	20.529	0.678	20.524	2.375
19	Tridecane	22.789	0.537	22.785	4.697



20	Tridecane, 6-methyl-	23.683	0.136	23.687	0.537
21	*Tridecane, 4-methyl-	---	---	23.828	0.343
22	*Tridecane, 3-methyl-	---	---	24.119	1.199
23	Tetradecane	24.575	0.882	24.574	5.292
24	Tetradecane, 3-methyl-	26.006	0.138	26.004	0.381
25	Pentadecane	26.721	2.747	26.719	4.25
26	*Pentadecane 4-methyl-	---	---	28.332	0.199
27	Decane, 5-propyl-	28.534	0.360	28.145	0.499
28	Hexadecane	29.833	3.233	30.048	0.236
29	*Dodecane, 2,6,11-trimethyl-	---	---	32.283	0.090
30	*Heptadecane, 2,6,10,15-tetramethyl-	---	---	32.969	0.696
31	Heptadecane	34.614	5.363	34.612	4.800
32	*Heptadecane 2-methyl-	---	---	38.380	0.640
33	Hexadecane, 3-methyl-	38.394	0.300	---	---
34	Octadecane	39.913	8.498	39.901	5.816
35	Hexadecane, 2,6,10,14-tetramethyl-	40.200	1.821	40.192	1.599
36	Pentatriacontane	43.315	0.427	43.310	0.130
37	Nonadecane	44.688	8.618	44.676	5.674
38	Eicosane	49.042	8.918	49.032	5.582
39	Octadecane,1-iodo	51.325	0.375	---	---
40	Henicosane	53.058	8.692	53.054	5.441
41	*Hentriacontane	---	---	55.741	0.389
42	Pentatriacontane	---	---	55.933	0.441
43	Docosane	56.814	8.455	56.809	5.977
44	Octacosane	59.352	1.233	59.341	0.844



45	Tetracosane	63.709	5.840	63.699	4.979
46	Hexacosane	70.103	0.664	70.103	0.055
Total concentration		92.719		87.892	
Olefins					
1	1-Hexene,2-methyl-	2.964	2.045	2.957	0.782
2	*2-Heptene, 2-methyl-	---	---	6.386	0.076
3	*1-Hexene, 2,3-dimethyl-	---	---	4.113	0.175
4	2-Pentene, 2,3,4-trimethyl-	5.409	0.087	5.493	0.410
5	*4-Nonene	---	---	10.530	0.307
6	2-Nonene	10.726	0.171	---	---
7	2-Decene, 5-methyl-,(Z)	19.089	0.086	19.086	0.950
8	*7-Tetradecene, (Z)	---	---	22.558	0.099
9	*9-Octadecene, €	---	---	24.808	0.112
10	1-Tetradecene	---	---	26.422	0.061
Total concentration		2.389		2.890	
Aromatics					
1	Toluene	4.969	0.633	4.951	1.160
2	Ethyl benzene	8.706	0.330	8.567	0.188
3	Benzene, 1,3-dimethyl-	8.954	0.421	8.941	1.386
4	Benzene, 1-ethyl-3-methyl-	13.094	0.328	13.083	0.208
5	*Benzene, 1,3,5-trimethyl-	---	---	13.676	1.444
6	Benzene, 1,2,4-trimethyl-	14.623	1.290	---	---
7	Benzene, 1-ethyl-2,3-dimethyl-	16.564	0.196	---	---
8	*Benzene 1-methyl-3-(1-methyl ethyl)	---	---	16.591	0.301
9	*Benzene, (1,1-dimethylpropyl)-	---	---	19.776	0.171



10	Naphthalene, 2,6-dimethyl	---	---	25.198	0.490
Total concentration		2.198			5.448
Naphthenes					
1	Cylohexene	2.858	0.264	2.850	0.093
2	Cylohexane, 1,1,3-trimethyl-	7.654	0.086	7.641	0.486
3	Cylohexane, propyl-	11.297	0.237	11.286	1.054
4	Cyclopentene,1-(2-methylpropyl)-	---	---	11.882	0.070
5	Cylohexane, 1-methyl, 3-propyl-	13.302	0.236	13.436	0.506
6	Cylohexane, butyl-	15.017	0.147	15.012	0.809
7	Cycloheptanone, 2-Methyl, 3-isopentyl-	58.417	1.011	---	---
8	Cyclododecane	24.123	0.713	---	---
9	*Undecane,2-cyclohexyl-	---	---	28.263	0.392
Total concentration		2.694%			3.48 %
Ester					
1	10-Undecanoic acid, 3-methyl butyl ester	---	---	64.792	0.281
Total concentration		0.281			

Similarly, percent differences for carbon number range distribution (CNRD) of the various hydrocarbons fall within the range of C₆-C₁₀, C₁₁-C₂₀ and C₂₁-C₃₅ in comparison with the original base oil were found to be 3.664, 13.877, and 17.541 %, respectively. As clear from the results presented in Fig.3.83, distinct changes have been undertaken in the carbon range of C₁₈-C₃₅ which is the area of interest because it lies within the lubricant range. The results indicated that this range is the most susceptible one to degradation for the base oil under study. The overall percent differences of the various carbon range hydrocarbons followed the same order as obtained in case of the original oil.



$$C_{18}-C_{35} > C_6-C_{10} > C_{11}-C_{20}$$

The overall percent difference in composition of the un-additized oxidized base oil in comparison with the control sample determined to be 9.370 % as per given results in Fig.3.84. It indicate that compositional change occurred leading to 9.370 % degradation level of the base oil under trial at 100 °C.

Table 3.21 shows a decline in concentration of the paraffins and corresponding increment was found in the concentration of the olefins, aromatics and naphthenes. The spectra in case of the fresh (un-oxidized) and the oxidized oils were found to be similar but with some differences in the concentration of paraffins as clear from the peak size of both of the chromatogram. The peak size of lower hydrocarbons of carbon content in the range of C_6-C_{11} in case of the un-oxidized oil is quite larger than the oxidized sample. Hydrocarbons of the aforementioned range may have been converted to aromatics via cyclization and dehydrogenation processes. Therefore, a prominent percent increase in the aromatic content of the oxidized oil was observed. The removal of labile H gives the ring enclosure to form naphthenes, the dehydrogenation of which might have promoted the aromatic ring formation [146].

Interestingly, there were some hydrocarbons that were included in the original composition, but found to be absent in the un-additized base oil oxidized at 100 °C as clear from the disappearance of peaks in the respective chromatograms. These were found to be 3-methyl hexadecane, iodo-octadecane (paraffins), 2-nonene, Z.E-7, 11-hexadecadiene-1-yl acetate (olefins), 1, 2, 4-trimethylbenzene, 1-ethyl, 2, 3-dimethylbenzene (aromatics) and 1-ethyl, 2-isopentyl cyclohexane and cyclododecane. Probably, these would have been converted to new aliphatic and aromatic hydrocarbons as a result of the oxidation at 100 °C.



Table: 3.21. Carbon Number Distribution of Original, Un-additized, RHE-and SDE-additized Base Oil Samples Oxidized at 100° C

Sample	Concentration (wt%)		
	C ₆ -C ₁₁	C ₁₂ -C ₁₇	C ₁₈ -C _n
Original oil	31.019	15.440	53.541
Un-additized oil	34.683	29.317	36.00
RHE-additized	29.663	19.125	51.212
SDE-additized	29.879	19.514	50.607

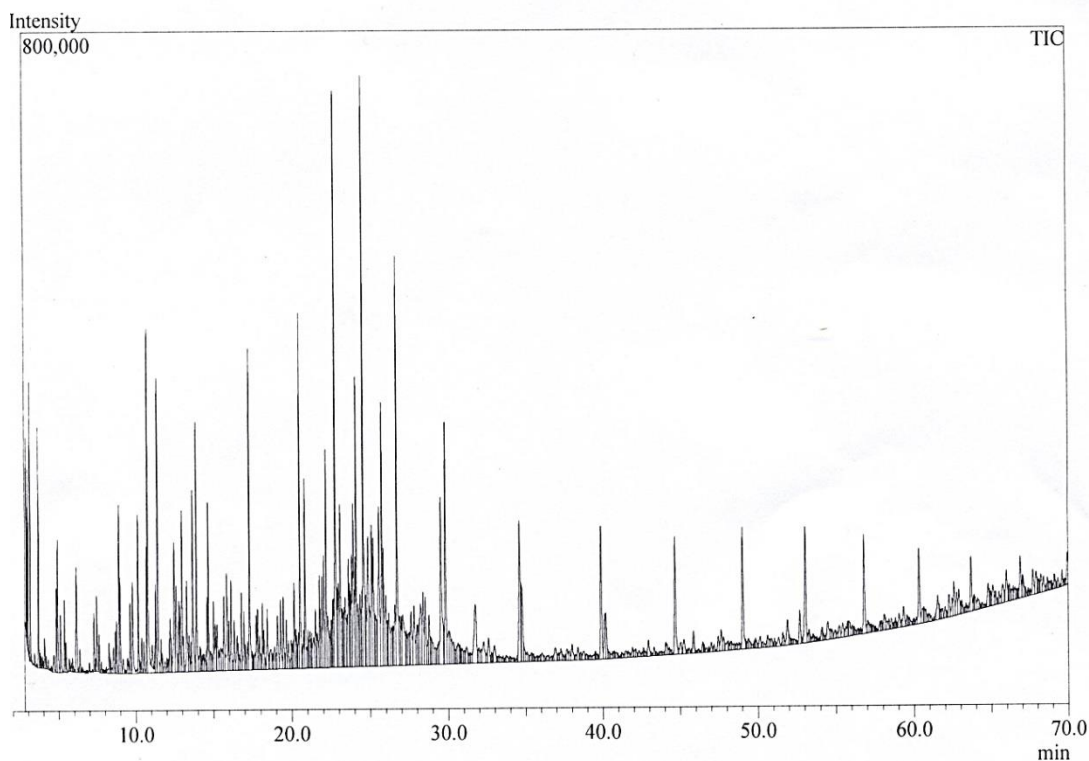


Fig.3.78. GC-MS chromatogram of un-additized MBO oxidized at 100 ° C



The additized samples oxidized under the aforementioned conditions were also analyzed. The GC-MS analysis data is presented in Table-3.22 and the corresponding chromatograms are given in Fig. 3.79 and Fig.3.80, respectively. The composition of the RHE and the SDE- additized samples contained similar classes of compounds as found in case of the original and un-additized samples.

The composition of the RHE-and the SDE-additized base oil samples was appeared to be in between the original base oil and the un-additized oxidized base oil, but more closer to the original oil as clear from the respective GC-MS chromatogram. However, the disappearance of a few and appearance of some new peaks can be observed in the corresponding profiles in case of the additized oxidized samples which may be as a result of the thermo-oxidative degradation. The hydrocarbons contents of the original oil and the new degraded products were confirmed from the change in their concentrations as given in the Table 3.22 in case of three-additized and the SDE-additized base oil samples.

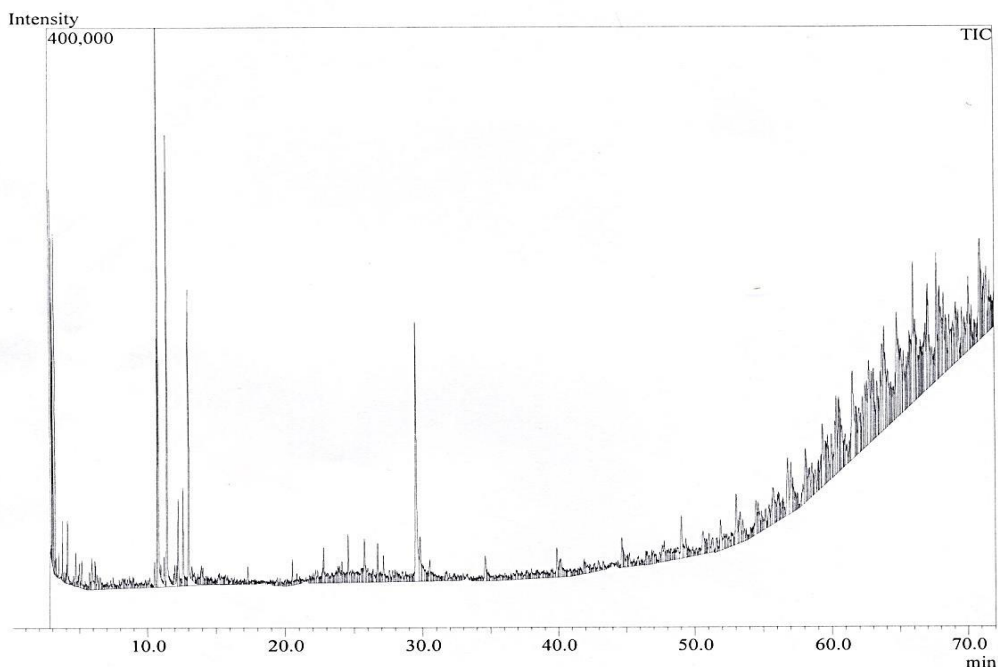


Fig.3.79. GC-MS chromatogram of RHE-additized MBO oxidized at 100 ° C

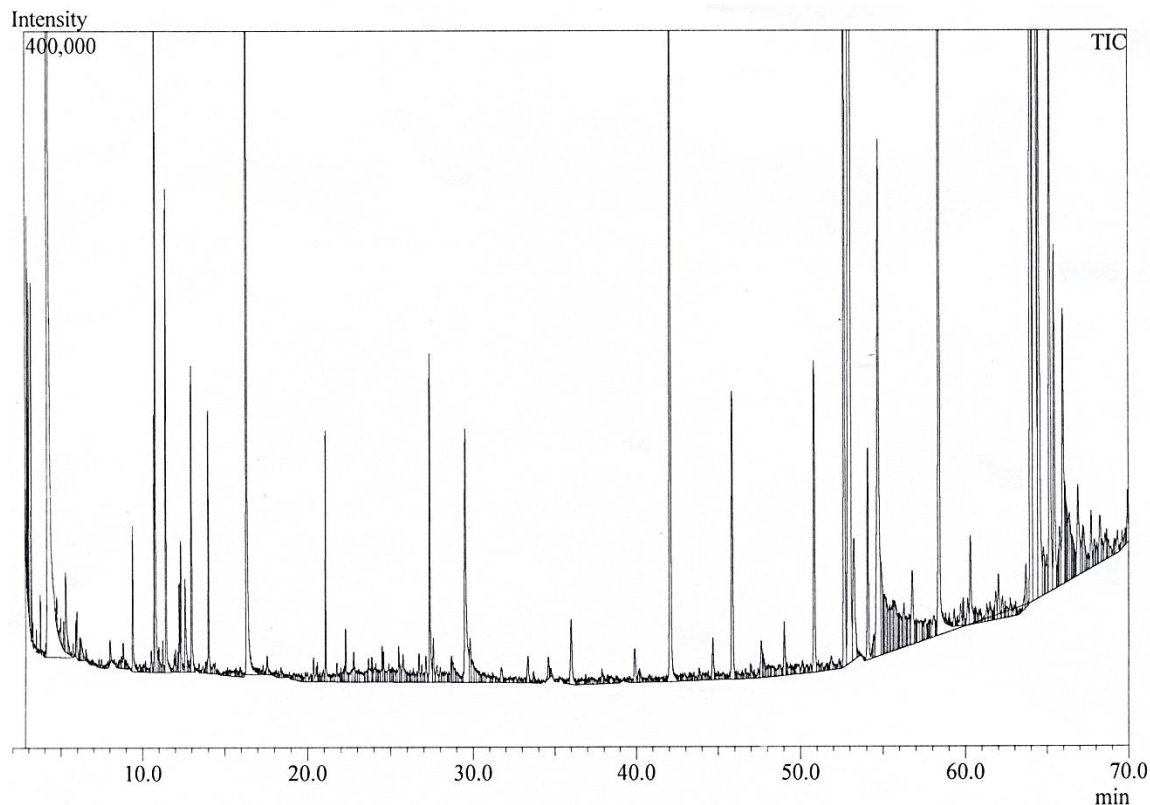


Fig.3.80. GC-MS chromatogram of SDE-additized MBO oxidized at 100 °C

In case of the RHE-additized base oil sample oxidized at 100 °C, the individual concentration of paraffins, olefins, aromatics, naphthenes and ester were found to be 91.927, 2.458, 2.877, 2.849 and 0.050 % and in case of the SDE-additized sample were found to be 90.972, 2.607, 3.277, 3.059 and 0.095 %, respectively as per results shown in Fig 3.81.

The hydrocarbons carbon range compounds confirmed (C_6 - C_{11} , C_{12} - C_{17} and C_{18} - C_{35}) in case of the RHE-additized sample were found to be, 29.663, 19.125 and 51.212 %, respectively. While the same hydrocarbons range compounds in case of the SDE-additized base oil sample were found to be, 29.879, 19.514 and 50.607 %, as per results presented in Table 3.21. As clear from the results, the lube oil range compounds (C_{18} - C_{35}) have been increased dominantly with the corresponding decrease in case of the un-additized oxidized base oil. While the lower range hydrocarbons (C_6 - C_{10} and C_{11} - C_{20}) have been reduced in comparison with the un-additized oxidized base oil.



The effectiveness of the RHE and SDE can be evaluated from the fact that both had maintained the lube oil range as required for a good lubricant which is C_{18} - C_{35} having 50 % concentration. The results indicate a decline in the level of degradation in case of the RHE-and SDE-additized base oil samples.

The nature of aliphatic and aromatic hydrocarbons of the RHE-and SDE-additized samples oxidized at 100 °C were also determined. The results are given in Table 3.21 which indicates a decline in the concentration of paraffins and corresponding increment in the concentration of the olefins, aromatics and naphthenes. The hydrocarbon net fractional composition of the RHE- and SDE-additized samples followed the order:

Paraffins > aromatics > naphthenes > olefins > ester

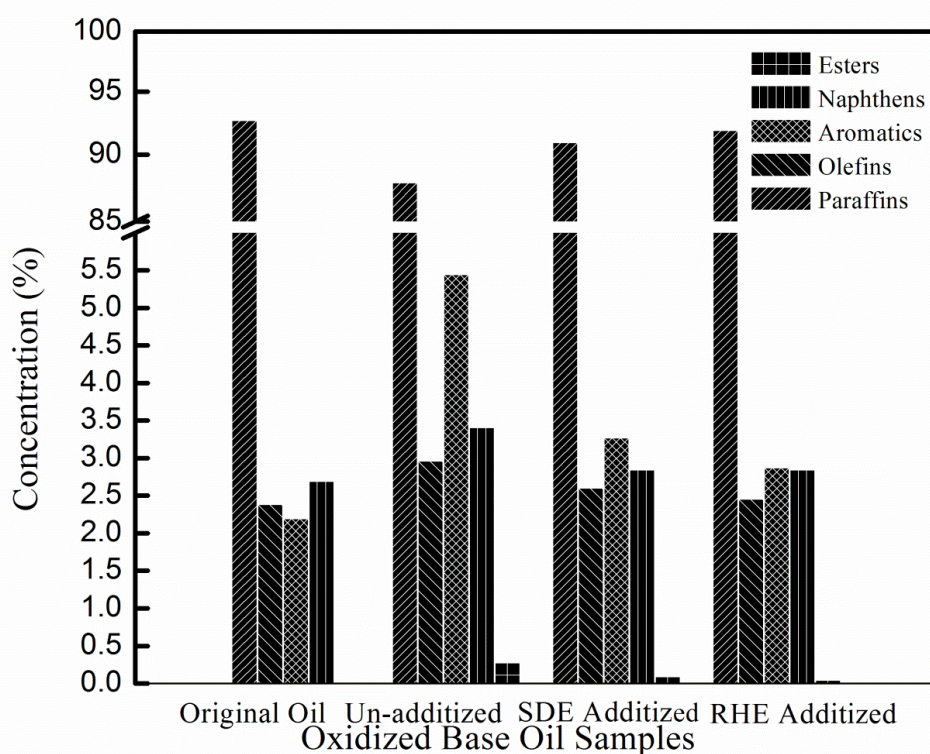


Fig.3.81. Concentration of hydrocarbon group types determined in un-additized, RHE-and SDE-additized base oil samples oxidized at 100 °C in comparison with the original base oil



In order to find out the antioxidant efficacy of the RHE and the SDE, the percent difference of their various fractions in comparison with the original base oil was also determined. The percent difference for the RHE-additized oxidized base oil in terms of concentration of paraffin, olefin, aromatic and naphthenes determined were found to be 0.792, 0.069, 0.679 and 0.155 %, respectively as shown in Fig 3.82. Similarly, in case of the SDE-additized sample, the distribution was found to be 1.747, 0.246, 1.079 and 0.957 %, respectively as per results given in Fig. 3.82.

Percent difference of the various hydrocarbons fall within the range of C_6 - C_{11} , C_{12} - C_{17} and C_{18} - C_{35} for the RHE- and SDE-additized oxidized sample were determined. The results are provided in Fig. 3.83. In case of the RHE-additized sample, the hydrocarbons in the above range were found to be 1.356, 3.685 and 2.329 % while in case of the SDE were found to be 1.140, 4.074 and 2.934 %, respectively when compared with the original oil. The results exhibited that values for the RHE-and SDE-additized samples are very much close to the original oil which indicate their antioxidant character. The values indicated that the RHE had increased the lube oil desired range to 15.212 % and SDE to 14.607 % with respect to the un-additized MBO.

The overall results of the carbon number range distributions evaluated that both of the antioxidants has avoided the thermo-oxidative degradation to a greater extent.

The level of degradation inhibited by the RHE and SDE can be evaluated from the percent decrease in the concentration of the main degraded (oxidized) product like ester between the additized and the un-additized oxidized base oil samples. The ester concentration determined in case of the un-additized oxidized sample was found to be 0.281 %, while in case of the RHE-additized sample was 0.050 % and in case of the SDE was 0.095 %. As clear from the results, both antioxidants have caused to reduce the concentration of the degraded products to a greater extent indicating their efficacy as antioxidants.

From all of the results, the percent differences determined in case of the RHE-additized sample with respect to the un-additized oil was found to be lower than in case



of the SDE-additized sample which can be attributed to the effectiveness of RHE than SDE at 100 °C.

The overall results showed that the RHE-and SDE- additized samples retained the composition of the original base oil accompanied by some changes that had occurred as result of the oxidation. The degraded compounds that were observed only in case of the un-additized base oil sample got distributed to some extent in case of the RHE-additized and SDE-additized samples. However, some compounds were found common in all of the three samples i.e. the un-additized, the RHE-and the SDE- additized base oil samples. Similarly, most of the compounds were found common but some showed differences between the original and the additized base oil samples.

Major similarity in the composition of the additized samples with the control indicated that these additives had maintained the originality of the oil to a greater extent.

Some degraded hydrocarbons that were appeared common in both of the RHE- and SDE- additized base oil samples were paraffins, olefins, aromatics, naphthenes and an ester as per results mentioned in Table.3.22. The Z.E, 7, 11-hexadecadien-2-isobutyl, cyclopenten-1-(2-methyl propyl), 2,6,11-trimethyl dodecane, 7- tetradecene, 2-methylheptadecane, hexacosane and pentatriacontane. Moreover, some degraded hydrocarbons were identified in the RHE-blend only which includes 1-tetradecene, 4-methylpentadecane, and pentacosane. Likewise, the SDE doped sample was characterized with some of the degraded products found to be 2,2-dimethylhexene, 4-nonene, 1,3,5-trimethyl benzene, 1-methyl-3-(1-methyl ethyl) benzene, 3-methylheptadecane and 2,6,12,15-tetramethylheptadecane. Only three degraded compounds were found in the RHE- additized sample in low concentration as compared with the SDE-additized sample which contained six compounds in high concentration. It is attributed to the low level of degradation and more effectiveness of the RHE as antioxidant compared with the SDE at 100 °C.

The RHE- and SDE-additized samples retained the composition of original sample in terms of the presence of some compounds that were totally absent in the un-additized oxidized samples. These compounds were 3-methylhexadecane, 1-



iodooctadecane and 1, 2, 4-trimethylbenzene. However, some compounds were characteristics of the RHE-additized sample which were found to be 1-ethyl, 2,3-dimethyl benzene, 1-ethyl,2-cyclohexyl and cyclododecane. The results indicate that the additized samples showed a significant level of resistance to degradation.

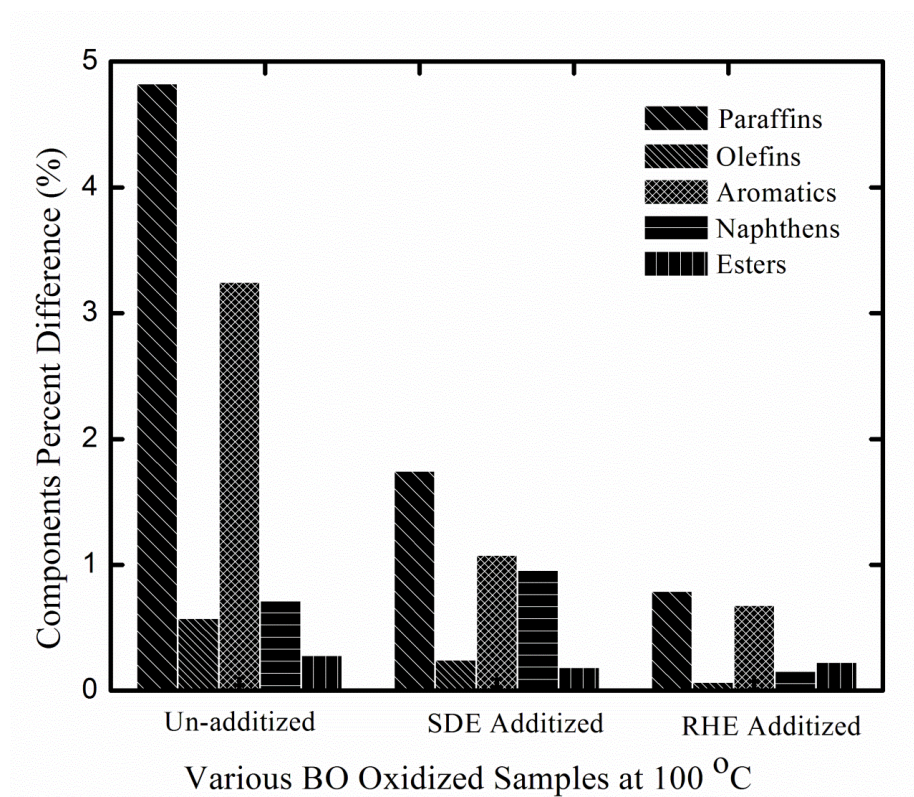


Fig.3.82. Percent difference in concentration of hydrocarbon group types determined in un-additized, RHE- and SDE-additized base oil samples oxidized at 100 °C

Thus, the sum of percent differences (overall % difference) for all of the fractions of the RHE-and SDE- additized samples including ester content with respect to the control sample were found to be 1.532 % and 4.124 %. The results showed that the base oil was degraded to 1.532 % in the presence of the RHE and to 4.124 % in case of the SDE-additized sample. These overall percent differences in case of the RHE and SDE were insignificant indicate their outstanding antioxidant behavior. While the overall percent difference for all of the hydrocarbon group types along with the ester content calculated in case of the un-additized oxidized oil in comparison with the original sample was significant (9.370 %) as clear from the results compiled in Tables 3.20 and 3.21. The

results reveal that overall, 9.370 % degradation (change in composition) occurred in case of the un-additized base oil which was declined to 1.532 and 4.124 % in the presence of the RHE and SDE, respectively as per results shown in Fig.3.84. Thus, the RHE reduced the degradation by 7.838 % and the SDE by 5.246 %. This significant reduction in the percent change in composition in case of the RHE and SDE-additized base oil samples reveal their outstanding and excellent antioxidant behavior.

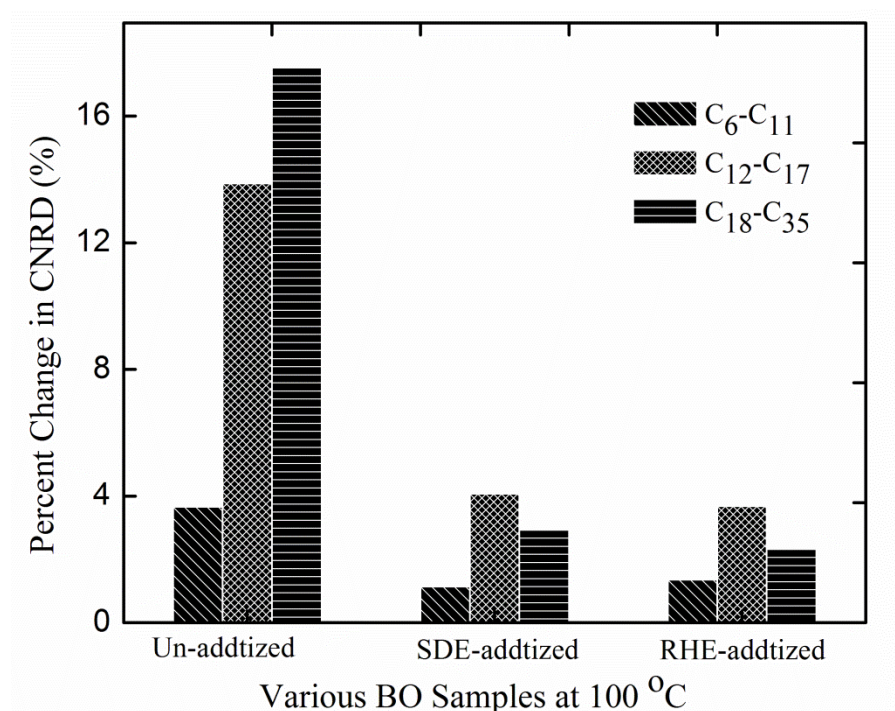


Fig.3.83. Percent difference in concentration of hydrocarbon carbon number range distribution determined in un-additized, RHE-and SDE- additized base oil samples oxidized at 100 °C

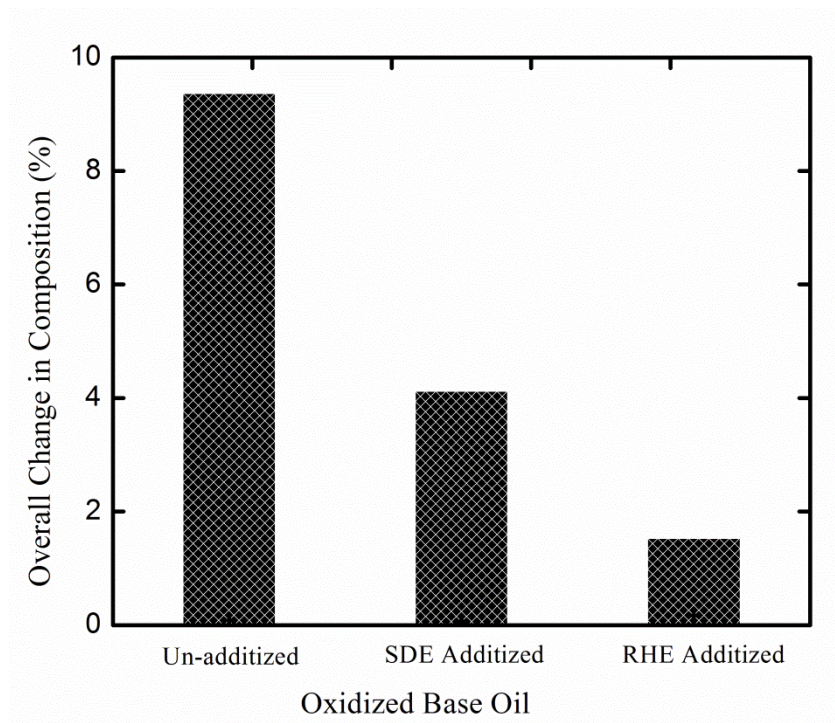


Fig.3.84. Overall change in chemical composition of the un-additized, RHE- and SDE- additized base oil samples oxidized at 100 °C

It was observed that the degradation of those hydrocarbons occurred which having carbon content $< C_{18}$. It is because of the fact that the concentration of hydrocarbons having carbon content $> C_{20}$ in case of the RHE- and SDE-additized samples was high than observed in case of the un-additized oxidized oil. The results revealed that the degradation will be completely avoided in case of the base oil having carbon content $> C_{18}$ by using these antioxidants.

**Table: 3.22. Individual Compounds Identified in RHE-and SDE-Additized Base Oil Samples Oxidized at 100 °C**

S. #	Compound	RHE Doped Sample		SDE Doped Sample	
		t _R	Con (%)	t _R	Con (%)
Paraffins					
1.	Heptane	2.961	2.039	3.154	2.010
2.	Octane, 2,5-dimethyl-	4.876	0.182	4.861	1.277
3.	Heptane, 3-methyl-	---	---	5.025	0.566
4.	Octane	6.187	0.724	6.162	1.515
5.	Octane, 4-methyl-	8.678	0.230	8.527	0.328
6.	Octane, 3-ethyl, 2,7-dimethyl	8.695	0.633	8.485	0.591
7.	Nonane	10.175	0.353	10.136	0.311
8.	Pentane, 3-ethyl-2,4-dimethyl-	10.789	12.764	10.427	13.627
9.	Octane, 2,6-dimethyl-	11.439	3.835	11.522	3.022
10.	Nonane, 2-methyl-	12.500	0.257	12.284	0.215
11.	Nonane, 3-methyl-	12.854	0.127	12.321	0.105
12.	Decane	13.625	0.576	13.921	0.451
13.	Octane, 2,3,6-trimethyl-	14.682	0.420	14.652	0.382
14.	Heptane, 2,5,5-trimethyl-	15.985	0.069	15.834	0.125
15.	Nonane, 3,7-dimethyl-	16.338	0.533	16.229	0.545
16.	Undecane	17.315	0.643	17.285	0.483
17.	Undecane, 5-methyl-	19.444	0.056	19.577	0.096
18.	Dodecane	20.525	0.673	20.631	0.869
19.	Tridecane	22.783	0.530	22.925	0.692
20.	Tridecane, 6-methyl-	23.675	0.129	23.735	0.234
21.	Tridecane, 4-methyl-	23.822	1.336		
22.	Tridecane, 3-methyl-	---	---	24.228	1.025
23.	Tetradecane	24.571	0.877	24.479	0.801
24.	Tetradecane, 3-methyl	26.001	0.132	26.025	0.220
25.	Pentadecane	26.715	2.743	26.630	2.439



26.	Pentadecane 4-methyl	28.285	1.156	---	---
27.	Decane, 5-propyl	28.530	0.350	28.255	0.397
28.	Hexadecane	29.828	3.226	30.754	3.111
29.	Dodecane, 2,6,11-trimethyl	32.279	0.082	32.112	0.053
30.	Heptadecane 2,6,10,15-tetramethyl	---	---	32.969	0.196
31.	Heptadecane	34.614	4.363	34.537	5.998
32.	Heptadecane 2-methyl-	38.380	0.050	38.377	0.041
33.	Hexadecane, 3-methyl	38.387	0.225	38.257	0.209
34.	Octadecane	39.906	8.492	39.826	8.213
35.	Hexadecane, 2,6,10,14-tetramethyl	40.194	1.817	40.148	0.989
36.	Tetratriacontane	43.311	0.425	43.316	0.412
37.	Nonadecane	44.684	8.613	44.609	7.534
38.	Eicosane	49.038	7.978	49.031	8.922
39.	Octadecane,1-iodo	51.321	0.339	51.321	0.339
40.	Henicosane	53.052	8.190	53.033	8.141
41.	Hentriacontane	---	---	---	---
42.	Pentatriacontane	55.913	0.065	55.811	0.051
43.	Docosane	56.810	8.448	56.726	7.812
44.	Octacosane	59.348	1.225	59.339	1.117
45.	Tetracosane	63.703	4.737	63.714	4.865
46.	Pentacosane	67.051	0.561	---	---
47.	Hexacosane	70.100	0.661	70.087	0.602
Total concentration		91.848		90.931	
Olefins					
1.	1-Hexene,2-methyl-	2.969	0.850	2.964	0.851
2.	1-Hexene, 2,3-dimethyl-	---	---	4.113	0.051
3.	2-Heptene, 2-methyl-	6.377	0.079	6.412	0.041
4.	2-Pentene, 2,3,4-trimethyl-	5.414	0.092	5.427	0.097
5.	4-Nonene	---	---	10.534	0.085



6.	2-Nonene	10.732	0.175	---	---
7.	Cyclopentene1-(2-methyl propyl-	11.878	0.035	11.863	0.025
8.	2-Decene, 5-methyl-,(Z)	19.093	0.089	19.098	0.093
9.	7-Tetradecene, (Z)	22.551	0.045	22.562	0.055
10.	9-Octadecene, (E)	---	---	----	---
11.	1-Tetradecene	26.415	0.033	---	---
12.	Z,E-7,11-Hexadecadiene-2-isobutyl	64.010	1.139	64.108	1.350
Total concentration		2.537		2.648	
Aromatics					
1.	Toluene	4.992	0.731	4.957	0.758
2.	Ethyl benzene	8.725	0.200	8.573	0.229
3.	Benzene, 1,3-dimethyl-	8.972	0.252	8.986	0.298
4.	Benzene, 1-ethyl-3-methyl-	13.245	0.145	13.257	0.168
5.	Benzene, 1,3,5-trimethyl-	---	---	13.682	1.104
6.	Benzene, 1,2,4-trimethyl-	14.754	0.222	14.749	0.212
7.	Benzene, 1-ethyl-2,3-dimethyl-	16.598	0.100	---	---
8.	Benzene 1-methyl-3-(1-methyl ethyl)	---	---	16.591	0.508
9.	Benzene, (1,1-dimethylpropyl)-	---	---	---	---
10.	Naphthalene, 2,6-dimethyl-	25.356	1.227		
Total concentration		2.877		3.277	
Naphthenes					
1.	Cylohexene	2.867	0.273	2.876	0.308
2.	Cylohexane, 1,1,3-trimethyl-	7.673	0.093	7.683	0.141
3.	Cylohexane, propyl-	11.352	0.245	11.249	0.299
4.	Cyclopentane,1-(2-methylpropyl)	---	---	---	---



5.	Cylohexane, 1-methyl, 3-propyl-	13.421	0.249	13.417	0.292
6.	Cylohexane, butyl-	15.117	0.156	15.122	0.195
7.	Cyclohexane, 1-Ethyl, 2-isopentyl	58.495	1.024	---	---
8.	Cyclododecane	24.186	0.720	24.181	0.833
9.	Undecane, 2-cyclohexyl	28.185	0.089	28.179	0.991
Total concentration 2.849					3.059
Ester					
1	10-Undecanoic acid, 3-methyl butyl ester	64.808	0.050	64.812	0.095
Total concentration 0.0500.095					
Grand Total			100		100

3.7.1.4. GC-MS Analysis of Various Base Oil Samples Oxidized at 200 °C for 06 Hours

GC-MS analysis of the various base oil samples oxidized at 200 °C for 06 h was also carried out. The GC-MS chromatograms are illustrated in Fig. 3.85-Fig.3.87 and the related GC-MS data is compiled in Table- 3.23.

The GC-MS chromatogram of the un-additized base oil oxidized at 200 °C for 06 h exhibited many weak, some medium and several intense peaks (1- 74 min) which indicate a complex mixture of compounds as shown in Fig.3.85. GC-MS data illustrated that the un-additized base oil sample comprised of a wide range of aliphatic and aromatic hydrocarbons as per results presented in Table 3.23. The chromatogram contains almost all of the peaks that were observed in case of the original and the un-additized base oil samples oxidized at 100 °C but with a changed intensity along with the appearance of some new bands. It indicates that the un-additized base oil sample oxidized at 200 °C contained all those constituents that were found in the original and un-additized base oil oxidized at 100 °C except some degraded products. The changed intensity of the peaks implies the different concentration of these compounds seen in case of the un-additized



oxidized sample when oxidized at 200 °C. The intensity of the bands responsible for the paraffins was reduced while the bands appeared for aromatics, naphthenes, olefins and ester get enhanced reveal their low and high concentration, respectively.

Thus, it may be derived that composition of the un-additized base oil was found to be the mixture of the original oil and the un-additized base oil oxidized at 100 °C. In spite of the similarity, a large number of new aliphatic and aromatic hydrocarbons were identified that would probably be formed due to the thermo-oxidative degradation at elevated 200 °C. The new compounds confirmed in comparison with the original oil were paraffins, olefins, naphthenes, aromatics and ester.

Among the new paraffins recognized, about 16 were found to be 3-methylheptane, 3,6-dimethylheptane, 2,7-dimethyl,3-ethyloctane, 3,7-dimethylnonane, 2-methyl-3-methylene nonane, 3-methylundecane, 3,9-dimethylundecane, 4-methyl tridecane, tetradecane, 3-methyl tridecane, 2,6,11-trimethyl dodecane, 2,6,10,15-tetramethyl heptadecane, 2-methyl heptadecane, 4-methyl pentadecane, hentriacontane, pentacosane and tritetracontane. These new paraffins collectively were recognized with a net concentration of 2.388 %.

Some olefins (6 new compounds) with overall 0.362 % concentration identified were found to be 1-heptene, 2,3-dimethyl 1-hexene, 2-undecen (E), 2-dodecene (E), 1-tetradecene and 9-octadecene (E). Six new aromatics recognized with the total concentration of 0.036 % were found to be 1,3,5-trimethyl benzene, 1-methyl-3-(1-ethyl methyl) benzene, 1,1-dimethyl propyl benzene, 1,8-dimethyl naphthalene, 2,6-dimethyl naphthalene and phenanthrene.

Three new naphthenes confirmed having concentration of 0.946 % were cyclododecane, 1,2,3-trimethylcyclohexane, and 2-cyclohexylundecane. While the carbonyl compound as oxidized degraded product found was 10-undecanoic acid, 3-methyl butyl ester.

Thus, the oxidized degraded composition mainly comprised of the constituents which were found to be mostly the ester, alkylated benzene and alkylated PAHs (di and



tricyclic), five and six membered alkylated naphthenes and some straight and branched olefins having carbon content C₆-C₁₆ [147].

The hydrocarbon group type distribution was also calculated from the GC-MS data which in turn used to investigate the overall change in composition of the various fragments of the oil under test. The relative abundance of the various hydrocarbons types contained the paraffins, olefins, naphthenes and aromatics calculated from GC-MS analysis as provided in Table 3.23. The proportions of the paraffins, olefins, aromatics, naphthenes and ester were found to be 81.0, 7.102, 3.657, 4.121 and 4.011 %, respectively as per data presented in Fig.3.88. The various hydrocarbons group type distribution determined in case of the un-additized oxidized base oil followed the order:

Paraffins>olefins>naphthenes>aromatics>ester

The various carbon range hydrocarbons were determined and the ranges were found to be C₆-C₁₁, C₁₂-C₁₇ and C₁₈-C₃₅. The concentrations of the aforementioned carbon range hydrocarbons calculated were found to be 52.962 % (C₆-C₁₀), 20.009 % (C₁₁-C₂₀) and 27.029 % (C₂₁-C₃₅), respectively as per results compiled in Table.3.24. Various carbon range compounds followed the order:

C₂₁-C₃₅>C₆-C₁₀>C₁₁-C₂₀

It was evaluated that the concentration of the long chain hydrocarbons range of C₂₀-C₃₅ (of the lubricant range) obtained was quite lower than obtained in case of the original base oil. The results indicated a greater level of degradation of both of the light and heavy hydrocarbons.

Likewise, at 200 °C, ester was confirmed as oxidized product found in the concentration of 4.011 %, which is found to be higher than the significant extent indicating the high level of degradation.

The percent differences of hydrocarbons group distribution between the original base oil (un-oxidized) and the un-additized oxidized base oil were determined as per data shown in Fig.3.89. These differences in terms of paraffin, olefin, and aromatic and



naphthenes contents were calculated and found to be 11.79, 4.713, 1.459 and 1.427 %, respectively.

In the same fashion, the percent differences for the various hydrocarbons in the carbon range of C_6 - C_{10} , C_{11} - C_{20} and C_{21} - C_{35} with respect to the original base oil were found to be 21.943, 4.569, and 26.512 %, respectively. The results implied that most prominent changes have been occurred in the carbon range of C_6 - C_{10} as clear from the results presented in Fig.3.90. It indicates that the hydrocarbons within this range are the most susceptible to degradation in case of the base oil under study.

The net percent difference in composition of the un-additized oxidized base oil in comparison with the control sample determined to be 19.389 % as per given in Fig.3.91. It indicates that compositional change had occurred leading to 19.389 % degradation level of the base oil under test at 200 °C. As clear from the data compiled in Table 3.23, a decline in the concentration of the paraffins and corresponding increment in the concentration of the olefins, aromatics and naphthenes was also found.

Level of degradation is associated with the increase in concentration of the naphthenes, olefins, aromatics or formation of new carbonyl compound like ester. The results of the oxidized product; ester accompanied by the percent increase in concentration of the olefins, aromatics and naphthenes revealed pronounced level of degradation.

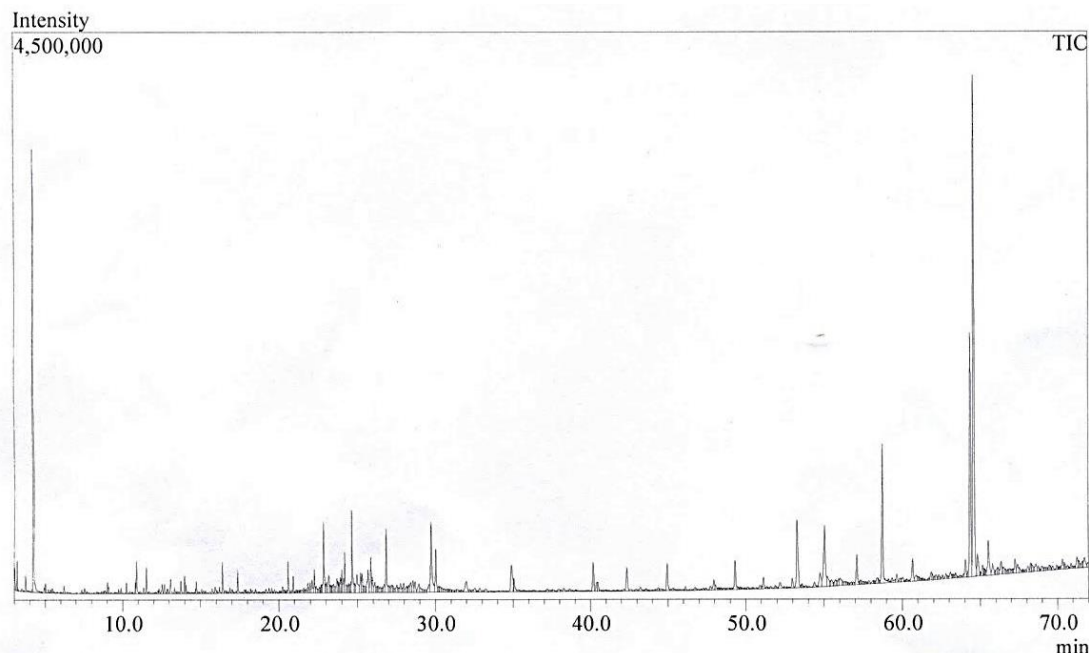


Fig.3.85. GC-MS chromatogram of un-additized MBO oxidized at 200 °C

Hydrocarbons of the C_6 - C_{11} range may have been converted to aromatics via cyclization and aromatization processes by Diels Alder mechanism [148]. Therefore, profound percent increase in the aromatic content of the oxidized oil was obtained. Similar to the un-additized oil at 100 °C, overall hydrocarbons of different carbon range hydrocarbons identified were found to be C_6 - C_{11} , C_{11} - C_{17} and C_{18} - C_{35} . It was observed that the concentration of the heavy hydrocarbons with in the range of C_{18} - C_{26} which lie in lubricant range was lesser than obtained in case of the original base oil. The results suggest that the degradation of the heavy hydrocarbons had also been undertaken.

The RHE- and SDE-additized base oil samples oxidized under the same conditions were also investigated. The respective GC-MS analysis data is presented in Table-3.23 and the corresponding chromatograms are given in Fig. 3.86 and Fig.3.87. The composition of these additized samples contained similar aliphatic and aromatic hydrocarbons as obtained in case of the original and the un-additized samples.

The composition of the RHE- and SDE-additized oxidized base oil samples was found to be in between the original and the un-additized oxidized base oil samples as clear from their GC-MS. The intensity of the peaks in case of the additized samples was



lesser compared to the un-additized oxidized base oil sample as shown in the corresponding chromatogram. The results suggest that the concentration of the compounds was found to be lower than the original and the un-additized oxidized oil sample as clear from the data compiled in Table 3.20. It is attributed to the oxidation of some amount of the paraffins that formed the degraded products to some extent in the presence of the RHE and SDE as antioxidants. Most of the individual compounds identified in case of the RHE-and SDE- additized oxidized base oil sample were appeared to be similar to the original un-oxidized oil sample. The results showed that the RHE- and SDE- additized samples had maintained the composition of the original base oil to some extent, however, some changes were occurred in the form of appearance of new peaks for compounds formed as a result of degradation.

In case of the RHE-additized oxidized base oil sample, the individual fraction concentration of the paraffins, olefins, aromatics, naphthenes and ester were found to be 89.382, 4.203, 2.003, 3.002 and 1.410 % and in case of SDE were 87.581, 4.442, 3.004, 3.320 and 1.653 %, respectively as per data presented in Fig.3.88.

To investigate the hydrocarbon group type compounds that had undergone degradation, the carbon range distribution of the RHE-additized and the SDE-additized samples oxidized at 200 °C was also determined. The results are given in Table 3.23 which indicated a reduction in the concentration of the paraffins and corresponding increment in the concentration of the olefins, aromatics and naphthenes. The hydrocarbons group distribution for the RHE-and SDE-additized samples was:

Paraffins>olefins>naphthenes>aromatics>ester

The hydrocarbons carbon range compounds recognized (C_6 - C_{10} , C_{11} - C_{20} and C_{21} - C_{35}) were found to be 27.489, 22.022 and 50.489 % in case of the RHE-additized sample. While the same hydrocarbons range compounds in case of SDE-additized base oil sample were found to be 29.977, 20.668 and 49.365 % as per results given in Table 3.24. The results exhibited that the hydrocarbons range compounds (C_6 - C_{11} and C_{12} - C_{17}) have been increased which were decreased in case of the un-additized oxidized base oil. The results



indicate a reduction in the level of degradation in case of the RHE-additized and the SDE-additized oxidized base samples.

Likewise, at 200 °C too, the RHE and SDE retained the lube oil range to the desired limit of 50 % which indicate a larger inhibition to degradation. The results suggest the excellent antioxidant role of the RHE and SDE at elevated temperature as well.

The percent differences in case of the RHE-additized sample in terms of concentration of the paraffin, olefin, aromatic and naphthenes configurations calculated with respect to un-additized sample were found to be 3.337, 1.814, 0.198 and 0.308 %, and for the SDE-additized sample were 5.138, 2.053, 0.806, 0.626 and 2.358 %, respectively as shown in Fig 3.89.

In order to evaluate the extent to which desired lubricant range hydrocarbons are conserved, percent differences of the various ranges including C_6-C_{11} , $C_{12}-C_{17}$ and $C_{18}-C_{35}$ hydrocarbons in case of the RHE-and SDE-additized oxidized sample were calculated. The results are provided in Fig. 3.90. In case of the RHE-additized sample, the percent difference for the above range hydrocarbons were found to be 3.530, 6.582 and 3.052 % while in case of the SDE were found to be 1.042, 5.228 and 4.176 %, respectively in comparison with the original oil. The results exhibited that values in case of the RHE-and SDE-additized samples were found to be close to the original oil which indicated their high thermo-oxidative stability.

The results also showed that RHE had increased the lube oil desired range to 23.460 % and the SDE to 22.336 % with respect to un-additized MBO.

The overall results of carbon number range distribution reflect their excellent antioxidant behavior because these prevented larger level of thermo-oxidation. However, based on results, the RHE was proved to be more associated with more antioxidant character than the SDE at 200 °C in terms of conserving the lube oil range from decomposition.



Thus, the sum of the percent differences (overall % difference) for all of the constituents of the RHE- and SDE- additized samples including ester content with respect to the control sample were found to be 8.245 and 10.981 % as per data illustrated in Fig.3.91. It revealed that the base oil was degraded to 8.245 % in the presence of the RHE and to 10.981 % in case of the SDE.

The overall percent differences in case of the RHE and SDE were insignificant indicate their outstanding antioxidant behavior. While the overall percent difference for all of the components along with the ester content calculated in case of the un-additized oxidized sample in comparison with the original sample was significant (19.389 %) as clear from Table 3.23.

Briefly, it revealed that overall 19.389 % degradation (change in composition) occurred in case of the un-additized base oil which was declined to 8.245 and 10.981 % in the presence of the RHE and SDE, respectively. Thus, the RHE reduced the degradation upto 11.144 % and the SDE up to 8.408 %. While the overall change in composition (degradation) of the base oil under study in case of their blends at 100 °C out of total was 19.389 %. This significant reduction in inhibiting the percent change in composition of the RHE-and SDE-additized samples revealed the outstanding and excellent antioxidant behavior, respectively.

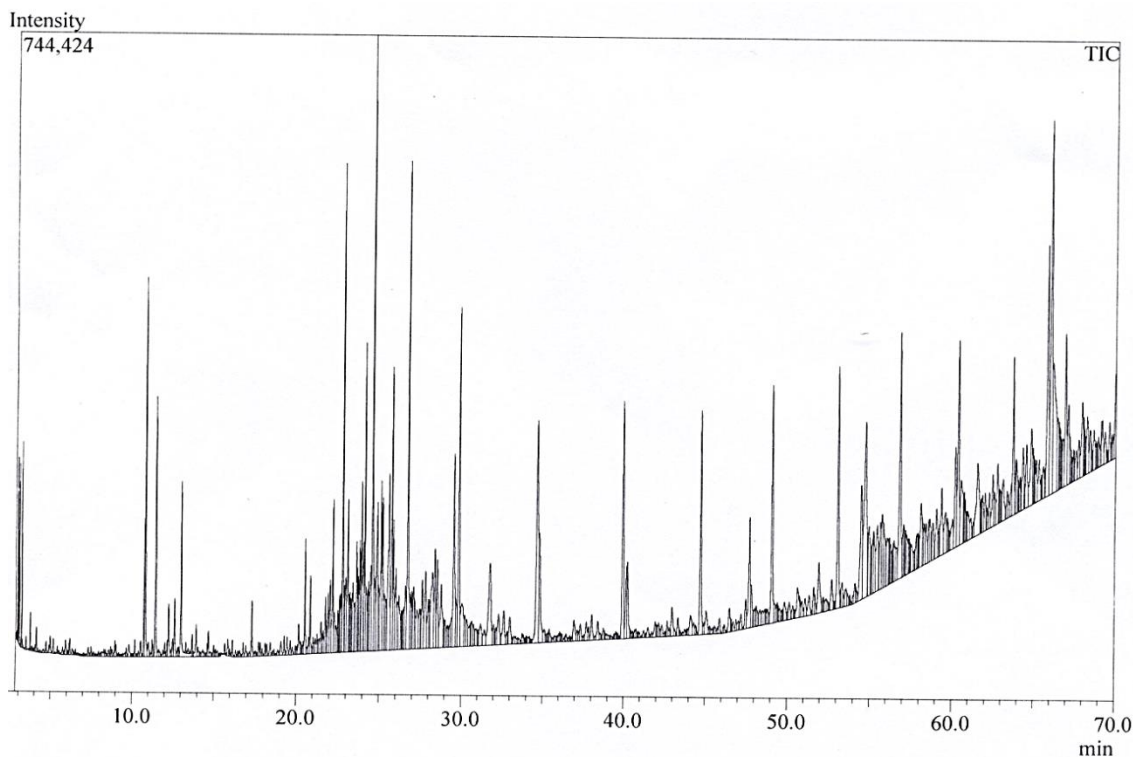


Fig.3.86. GC-MS chromatogram of RHE-additized MBO oxidized at 200 °C

The degree of degradation prevented by the RHE and SDE can be analyzed from the percent decrease in the concentration of the undesired degraded (oxidized) products like ester between the additized and the un-additized oxidized base oil samples. The ester concentration determined in case of the un-additized oxidized sample was found to be 4.011 %, for the RHE-additized samples was 1.42 % and SDE was 1.653 %. As clear from the percent differences of degraded products, both of the antioxidants have declined the concentration of the degraded products to a greater extent indicating their efficacy level as antioxidants.

The intensity of the peaks of degraded products (aromatics, olefins, naphthenes and ester) was found larger than determined in case of the RHE-and SDE- additized base oil samples oxidized at 100 °C. It indicate the lesser thermo-oxidative stability of the RHE and the SDE at 200 °C as compared with 100 °C.

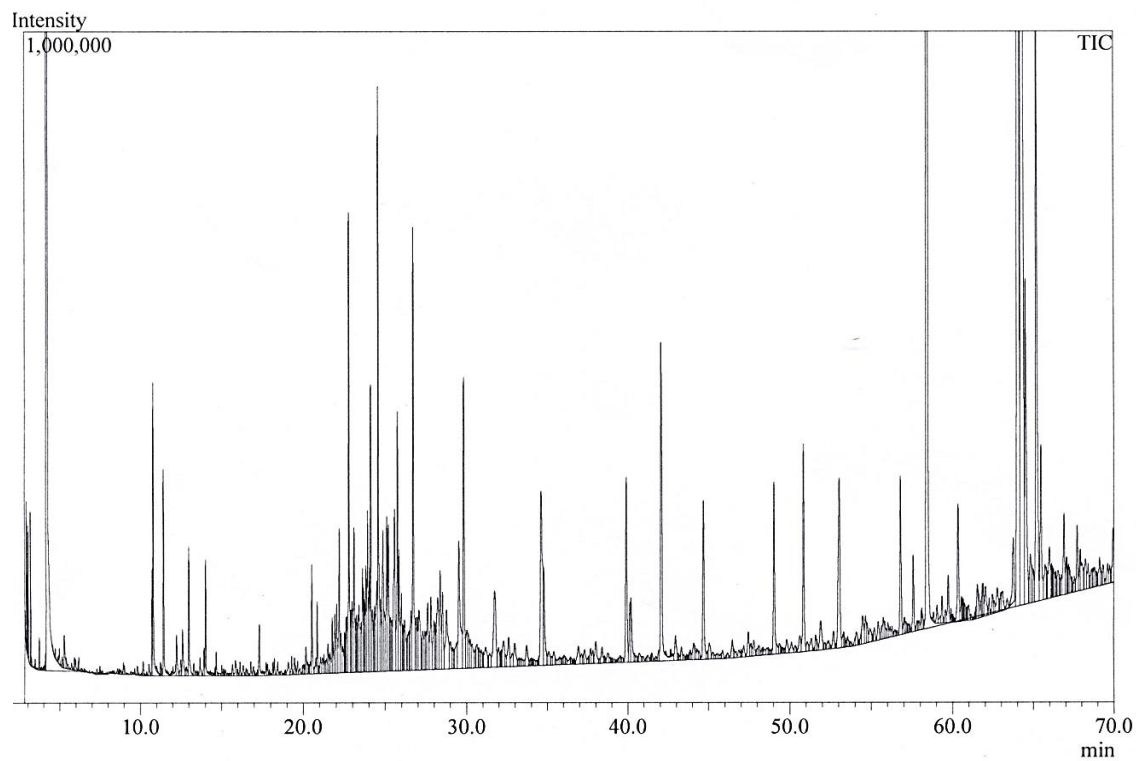


Fig.3.87. GC-MS chromatogram of SDE-additized MBO oxidized at 200 °C

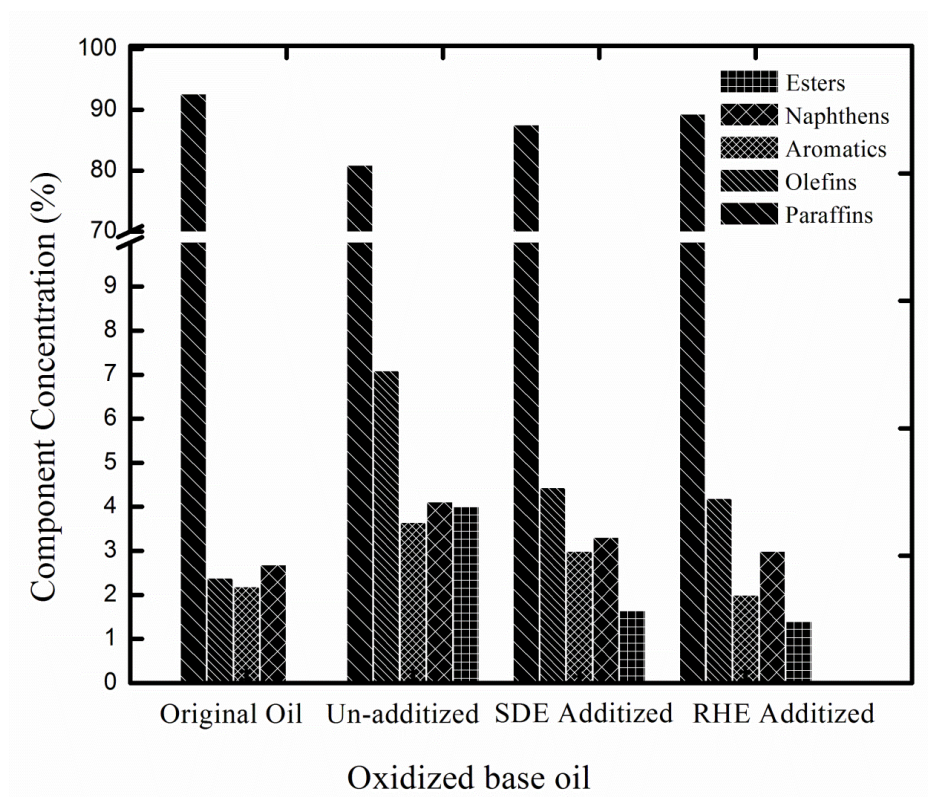


Fig.3.88. Concentration of various hydrocarbon group types determined in un-additized, RHE-and SDE- additized base oil samples oxidized at 200 °C in comparison with original base oil

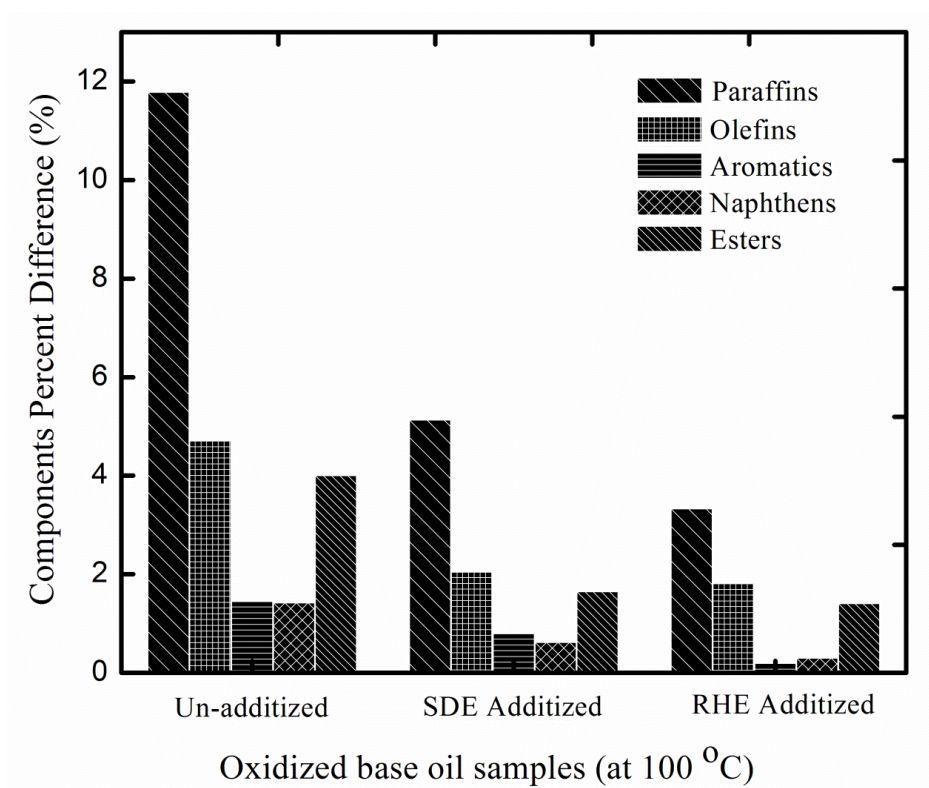
Some common degraded hydrocarbons found in case of both of the RHE and the SDE blends were paraffins, olefins, aromatics, naphthenes and an ester. These were 3-methylheptane, 2,6-dimethyloctane, 3,7-dimethylnonane, 2,6-dimethyl undecane, 2,6,11-trimethyl dodecane, cyclododecane, 1,2,3-trimethyl cyclohexane and 2-cylcohexyl undecane, Moreover, the intensity of these aforementioned degraded compounds peaks in case of the RHE- additized sample was found to be smaller than the SDE- blend. The results signify the more efficient antioxidant behavior of the RHE at 200 °C similar to 100°C than the SDE.

Among the degraded compounds that were recognized in the un-additized sample, some were appeared in the RHE and some in SDE-additized samples. Thus, the RHE blend contained compounds such as 4-methyltridecane, 4-methylpentadecane, pentacosane, 1-tetradecene and 2,3-dimethyl benzene. Likewise, the SDE-additized



samples after oxidation comprised of the degraded compounds like 3-methyltridecane, 2,6,10,15-tetramethyl heptadecane, 2,3-dimethyl-1-heptene, 1,3,5-trimethyl benzene and 1-methyl-3-cyclohexyl benzene.

The antioxidant proficiency of the RHE and SDE was evaluated in terms of determining the percent difference of the various fragments of the un-additized and the additized samples in comparison with the original sample.



3.89. Percent difference in hydrocarbon group types in RHE- and SDE-additized base oil samples oxidized at 200 °C in comparison to un-additized base oil samples

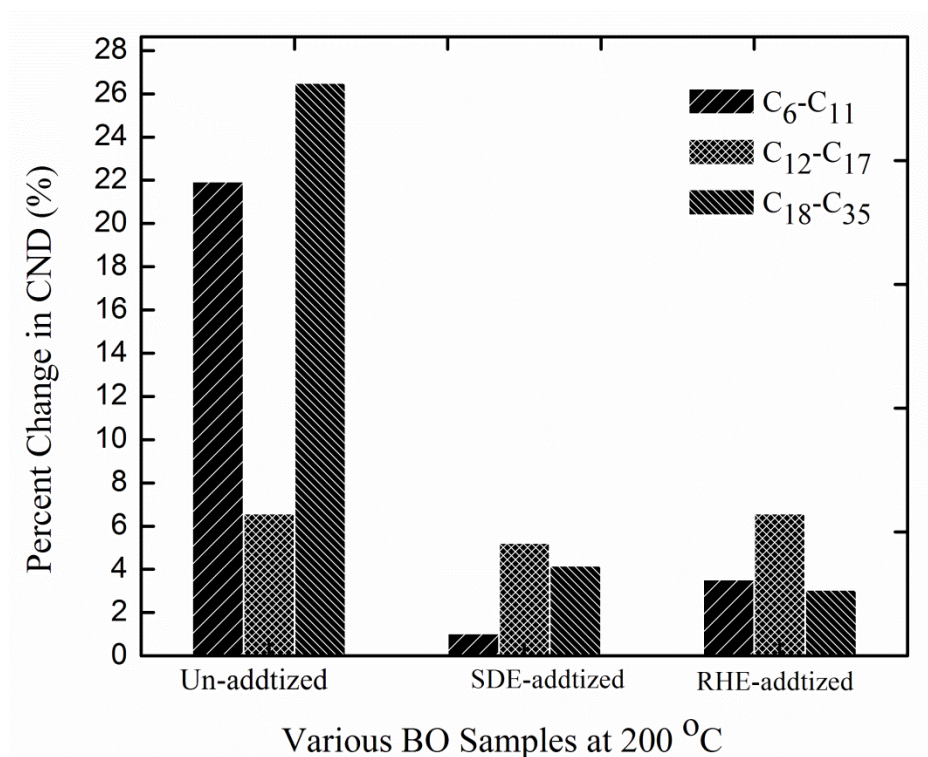


Fig.3.90. Percent difference in concentration of hydrocarbon carbon number range distribution determined in un-additized, RHE- and SDE- additized base oil samples oxidized at 200 °C

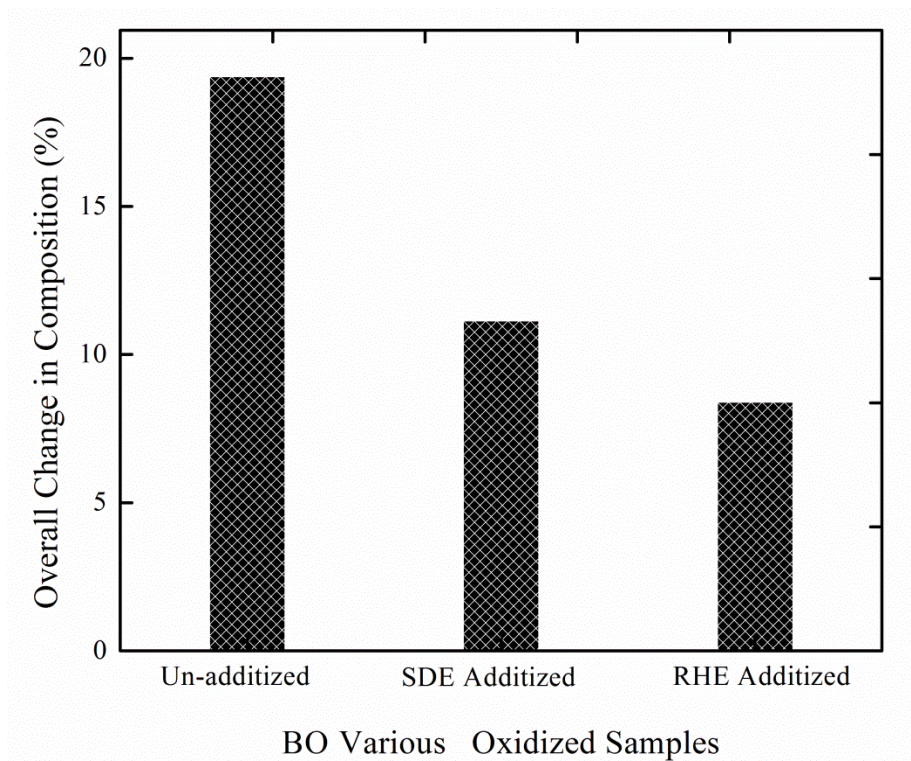


Fig. 3.91. Overall change in composition of un-additized, RHE- and SDE-additized oxidized base oil samples at 200 °C

It was thus evaluated that degradation of those hydrocarbons occurred having carbon content $< C_{20}$. It is because, the concentration of the hydrocarbons having carbon content $> C_{20}$ for the RHE- and SDE-additized samples was higher than observed in case of the un-additized oxidized oil. The results revealed that degradation will be avoided to a greater extent in case of the base oil having carbon content $> C_{20}$ by using these antioxidants.

**Table: 3.23. Individual Compounds Identified in Un-additized, RHE- and SDE- Additized Base Oil Samples Oxidized at 200°C**

S.#	Compound	Un- Additized		RHE- Additized		SDE- Additized	
		t _R	Con (%)	t _R	Con (%)	t _R	Con (%)
Paraffins							
1	Heptane	3.189	0.730	---	---	---	---
2	2,5-Dimethyloctane	4.233	14.685	4.249	8.139	4.251	8.825
3	2,6-Dimethyloctane	---	---	4.892	0.611	4.896	0.623
4	Heptane, 3-methyl-	5.194	0.111	5.223	0.045	5.225	0.561
5	Octane	6.239	0.294	6.266	0.606	6.263	1.390
6	Octane, 4-methyl-	8.757	0.105	8.732	0.107	8.412	0.278
7	Octane, 3-ethyl, 2,7-dimethyl	8.841	0.111	8.761	0.502	8.532	0.414
8	3,5-Dimethylheptane	8.993	0.028	9.067	0.315	9.089	0.271
9	Nonane	10.237	0.388	10.028	0.245	10.073	0.187
10	Pentane, 3-ethyl-2,4-dimethyl	10.892	2.746	10.793	12.613	10.572	10.385
11	Nonane, 2-methyl-	12.566	0.255	12.325	0.116	12.218	0.181
12	Nonane, 3-methyl-	12.929	0.136	12.623	0.082	12.421	0.088
13	Decane	13.999	0.621	13.665	0.452	13.872	0.327
14	2,3,6-Trimethyloctane	14.756	0.362	14.596	0.389	14.531	0.258
15	2,5,5-Trimethylheptane	16.065	0.094	15.863	0.078	15.839	0.092
	Nonane, 3,7-dimethyl	16.216	0.131	16.341	0.433	16.324	0.349
17	2-Methyl, 3-methylenenonane	17.120	0.018	---	---	---	---
18	Undecane	17.399	0.816	17.223	0.582	17.242	0.428
19	Undecane, 5-methyl-	19.548	0.143	19.397	0.048	19.593	0.079
20	Undecane, 3-methyl-	19.744	0.103	---	---	---	---
21	Dodecane	20.608	0.997	20.578	0.625	20.616	0.845
22	2, 6-	20.929	0.603	20.942	0.511	20.958	0.556



	Dimethylundecane						
23	3, 9-Dimethylundecane	22.957	0.026	---	---	---	---
24	Tridecane	22.863	1.946	22.799	0.568	22.949	0.662
25	Tridecane, 6-methyl-	23.763	0.205	23.698	0.101	23.777	0.203
26	Tridecane, 4-methyl-	23.906	0.130	23.836	0.286	---	---
27	Tridecane, 3-methyl-	24.122	0.262	---	---	24.288	1.003
28	Tetradecane	24.662	2.560	24.496	0.807	24.495	0.778
29	Tetradecane, 3-methyl	26.117	0.168	26.028	0.093	26.122	0.186
30	Pentadecane	26.846	2.422	26.733	2.690	26.621	2.375
31	Decane-5-propyl-	28.296	0.210	---	---	---	---
32	Pentadecane 4-methyl-	28.493	0.109	28.296	0.168	---	---
33	Hexadecane	30.020	2.224	29.849	4.191	30.781	4.066
34	Dodecane, 2,6,11-trimethyl-	32.525	0.046	32.289	0.055	32.124	0.041
35	Heptadecane, 2,6,10,15-tetramethyl	33.229	0.126	---	---	32.992	0.163
36	Heptadecane	35.058	0.526	34.634	7.317	34.561	5.915
37	Heptadecane 8-methyl	37.192	0.187	38.396	0.071	38.395	0.041
38	Heptadecane 2-methyl	38.229	0.159	---	---	---	---
39	Heptadecane 3-methyl	38.660	0.110	38.411	0.182	38.289	0.153
40	Octadecane	40.177	2.031	39.842	7.490	39.783	7.226
41	Tritetracontane	40.468	0.408	---	---	---	---
42	Hexadecane, 2,6,10,14-tetramethyl-	40.468	0.408	40.198	1.801	40.159	0.957
43	Tetratriacontane	43.235	0.171	43.326	0.387	43.325	0.385
44	Nonadecane	44.952	1.857	44.698	7.574	44.579	7.494
45	Eicosane	49.316	1.871	49.023	8.918	49.042	7.891
46	Octadecane, 1-iodo	51.608	0.079	51.333	0.302	51.336	0.308
47	Henicosane	53.341	2.327	53.063	7.635	53.043	7.105
48	*Hentriacontane	55.733	0.207	---	---	---	---
49	Pentatriacontane	56.029	0.360	55.935	0.049	55.827	0.059



50	Docosane	57.107	1.792	56.828	7.419	56.738	6.788
51	Octacosane	59.808	0.172	59.357	1.185	59.348	1.104
52	Tricosane	64.034	0.986	63.714	5.713	63.722	4.784
53	Tetracosane	64.597	0.986	64.613	0.990	64.611	0.988
54	Pentacosane	67.397	0.413	67.069	0.138	---	---
55	Hexacosane	70.427	0.391	70.110	0.635	70.099	0.569
Total concentration			81.00		89.382		87.581
Olefins							
1	1-Hexene,2-methyl-	2.988	0.261	2.977	0.850	2.971	0.851
2	1-Heptene	2.988	0.261	---	---	---	---
3	1-Hexene, 2,3-dimethyl	4.160	0.022	---	---	4.118	0.051
4	2-Pentene, 2,3,4-trimethyl	5.552	0.079	5.419	0.092	5.438	0.097
5	2-Undecene (E)	17.904	0.022	---	---	---	---
6	2-Dodecene (E)	17.904	0.022	---	---	---	---
7	2-Decene, 5-methyl-, (Z)	19.183	0.206	19.111	0.089	19.105	0.093
8	9-Octadecene, (E)	24.395	0.023	---	---	----	---
9	1-Tetradecene	26.547	0.012	26.422	0.033	---	---
10	Z,E-7,11-hexadecadiene-1-yl-acetate	64.356	6.195	64.010	3.139	64.115	3.350
Total concentration			7.102		4.203		4.442
Aromatics							
1	Toluene	5.013	0.605	4.997	0.731	4.961	0.758
2	Ethyl benzene	8.638	0.135	8.727	0.200	8.575	0.229
3	Benzene, 1,3-dimethyl-	9.015	0.643	8.979	0.552	8.989	0.598
4	Benzene, 1-ethyl-3-methyl-	13.165	0.093	13.248	0.145	13.260	0.168
5	Benzene, 1,3,5-	13.759	0.644	---	---	13.685	0.804



	trimethyl-						
6	Benzene, 1,2,4-trimethyl-	14.702	0.174	14.755	0.222	14.749	0.212
7	Benzene, 1-ethyl-2,3-dimethyl-	16.589	0.077	16.606	0.100	---	---
8	Benzene 1-methyl-3-(1-methyl ethyl)	16.681	0.104	---	---	16.591	0.050
9	Benzene, (1,1-dimethylpropyl)-	19.871	0.079	---	---	---	---
10	Naphthalene, 1,8-dimethyl-	25.213	0.599	25.221	0.123	25.218	0.165
11	Naphthalene, 2,6-dimethyl-	25.308	0.468	---	---	---	---
12	Phenanthrene	39.056	0.036	---	---	---	---
Total concentration			3.657		2.003		3.004
Naphthenes							
1	Cylohexene	2.881	0.034	2.875	0.294	2.886	0.328
2	Cylohexane, 1,1,3-trimethyl-	7.707	0.085	7.685	0.112	7.691	0.165
3	Cyclopentane, 1-butyl, 2-ethyl	8.344	0.067	---	---	---	---
4	Cylohexane, propyl-	11.359	0.181	11.392	0.262	11.263	0.323
5	Cylohexane, 1-methyl, 3-propyl-	13.371	0.284	13.429	0.273	13.425	0.319
6	Cylohexane, butyl-	15.092	0.149	15.128	0.171	15.131	0.216
7	Cyclohexane, 1-Ethyl, 2-isopentyl-	---	---	58.514	0.044	---	---
8	Cyclododecane	24.662	2.560	24.195	1.738	24.181	1.833
9	Undecane, 2-cyclohexyl-	28.419	0.158	28.197	0.108	28.179	0.136
Total concentration			4.121		3.002		3.320
Ester							
1	Octanoic acid, isopentyl ester	64.597	4.011		1.410		1.653
Total concentration			4.011		1.410		1.653
Grand Total			100		100		100

**Table 3.24 Carbon Number Distribution of Original and Various Base Oil Samples Oxidized at 200° C**

Oil Sample	Concentration (wt%)		
	C ₆ -C ₁₁	C ₁₂ -C ₁₇	C ₁₈ -C _n
Original	31.019	15.440	53.541
Un-additized	52.962	20.009	27.029
RHE-additized	27.489	22.022	50.489
SDE-additized	29.977	20.668	49.365

CONCLUSIONS

The following conclusions can be drawn:

- Physico-chemical properties were chosen in order to decide about the experimental conditions for significant oil degradation. The percent changes in viscosity characteristics and complementary properties indicate that maximum oil was degraded in oxidation time interval of 00-6h followed by 12-18h, followed by 6-12h and followed by 18-24h at 100 °C in case of LTO experiments and 200 °C in case of HTO experiments.
- Based on the appearance of some new peaks in FTIR analysis corresponded to oxidized products like naphthenes, olefins, aromatics, & esters in the un-additized oxidized base oil samples compared with the additized samples and the differences in PAI & PH parameters calculated for C=O and C=C bands, both RHE and SDE proved to be effective antioxidants.
- Comparison of the conductimetric analysis of the original and variously oxidized samples in terms of oxidation induction time (OSI) & SF values revealed the antioxidant character of both RHE and SDE.
- The oxidative and thermal stabilities of the original and various oxidized samples determined by TGA in terms of T_{onset}, T_{off set}, fast volatiles, weight gain and their comparison in terms of % differences indicated thermal stabilities of the additized samples.



- The isothermal calorimetric analysis in terms of oxidation induction time (OIT) and the insignificant percent differences of the additized samples with the original base oil indicated the antioxidant character of the RHE and SDE.
- The mass spectrometric-chromatographic analysis in terms of changes in individual compounds, carbon range and hydrocarbon group type distributions indicated stabilities of the additized samples compared to un-additized oil which has established the antioxidant activities of the RHE and SDE.
- Upon comparing the efficiency of the two antioxidants used among themselves, overall antioxidants performance of the RHE can be ranked as outstanding at 100°C & excellent at 200°C and SDE as excellent at 100°C & better at 200 °C.
- Both of the antioxidants could be used on commercial scale in lubricating oil formulation to eliminate the use of costly and environmentally objectionable additives.



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