République algérienne démocratique et populaire
Ministère de l'enseignement supérieur et de la recherche scientifique
Université A. Mira de Bejaia

Faculté de Technologie
Département de Génie des procédés
Laboratoire LMPA

Mémoire

EN VUE DE L'OBTENTION DU DIPLOME DE
Master

Domaine : Science et Technologie   Filière : Génie des Procédés
Spécialité : Génie Chimique

Présenté par

Nkoko Limakatso Vivian

Thème

A Characterisation Study of Thermo-Oxidation of Lubricant Oil of an Automotive Engine

Soutenue le 01 /07 /2024   **Devant le jury composé de :**

Nom et Prénom	Grade	Affiliation	Qualité
Mr Zembouai Idris	**MCA**	Université de Bejaia	Président
Mme Lynda Zaidi	**MCB**	Université de Bejaia	Examinateur
Prof. Mustapha Kaci	**PR**	Université de Bejaia	Encadrant
Dr. Celia Idres	**DR**	Université de Bejaia	Co- Encadrant

Année Universitaire : 2023/2024

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my supervisor, Prof. Mustapha Kaci, for his invaluable guidance, support and insightful feedback throughout the process of constructing this work. His expertise and positive critique have been a valuable building material in completing this work.

I am also greatly thankful to my co-supervisor Dr Celia Idres, for her patience, advice, valuable input and fostering a conducive environment for carrying out my experimental work. Her guidance has significantly enriched the quality of this work.

I am indebted to the University of Bejaia as well as the government of Algeria for offering me this golden opportunity to pursue my studies, whilst also providing the necessary resources to carry out this work.

My heartfelt appreciation to the entire Nkoko and Selebeleng family for their prayers, financing my education, for their support emotional as well as their endless love and encouragement through this journey. To my friends, I am so thankful for moral support for they have eased the burden showing up every time I needed them throughout my academic journey. And to everyone who contributed to the writing of this work, I appreciate every single effort.

Above all, I thank the Almighty God, Abba Father, the Alpha and Omega, He who was with me from the beginning and His grave sustained me thus far. We plan but He executes so in the end all glory belongs to Him.

DEDICATIONS

I dedicate this work to my amazing grandmother, Mookho Annie Selebeleng. For holding my hand every single step of my life, her wisdom and love have been the guiding light in my life. I am immensely grateful for her unwavering support and prayers for they have brought me this far. Kea leboha Mots'oeneng oa ha Khiba!

I also dedicate this work to the memory of my late brother, Lebohang Kamohelo Nkoko, whose encouragement, love and support remains an inspiration in my life. Robala ka Khotso Mots'oeneng.

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LIST OF ABBREVIATIONS

LOs: LUBRICANT/ LUBRICATING OILS

SAE: SOCIETY OF AUTOMOTIVE ENGINE

ISO: INTERNATIONAL ORGANISATION FOR STANDARDIZATION

FTIR: FOURIER TRANSFORM INFRARED SPECTROSCOPY

UV-VISIBLE: ULTRAVIOLET VISIBLE SPECTROSCOPY

Mt: MILLION TONNES

API: AMERICAN PETROLEUM INSTITUTE

ASTM: AMERICAN SOCIETY FOR TESTING MATERIALS

DAO: DEASPHALTED OIL

PAO: POLYALPHAOLEPHIN OILS

TAN: TOTAL ACID NUMBER

VOCs: VOLATILE ORGANIC COMPOUNDS

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GENERAL INTRODUCTION

The lubricating oil of an automotive engine is one of the leading sectors contributing to the general global market being significant in manufacturing industries such as the automotive, chemical plant and food processing. It is utilised for the protection of production machines to prevent wear, tear, rust and corrosion between the metals therefore contributing positively to the life span of the machine. In this study we will be focusing mainly on the application of automotive engine oil which used by motorcycles and vehicles. Their automotive engine are the core component of a vehicle responsible for converting fuel into mechanical energy to propel the vehicle. Therefore, to carry out their function well, they require the use of LOs, which ensures the efficiency, and effectiveness of an engine. Not only does it improve the efficiency of the engine but also prolong its durability. For this central role that LOs play in the production sector, it is thus important to ensure their availability and sustainability. With an increase in population, the demand for automotive cars is also high thus; the need for maintenance of their engine requires the use of LOs. According to Carolina Tavares Pinherio, in 2016, the world market of lubricating oil was estimated to be 35.7 Mt accounting to 42% of the global market. Asia Pacific had the highest share and fasted growing consumption of LOs. Meanwhile Europe accounting for the 19% of the demand of lubricating oil, consuming 6.8 Mt every year [1]. Nowadays, Asia-Pacific is still said to be the largest regional market for lubricants and fuel additives. In 2023, the Asia-Pacific market reached a combined value of 6.99 billion U.S. dollars out of a global total of 19.6 billion U.S. dollars. It is expected to remain the largest regional market throughout the next decade. Furthermore, it is projected that the region will maintain its position throughout the next decade. In addition China and India have the greatest automobiles on the road thus confirming the high demand for lubricant oils [2]. In Africa, there is also a rapid growth in demand of LOs, the market is projected to reach 2.65 billion litres in 2024 and is anticipated to grow to 2.84 billion litres by 2026 [3]. In 2020, the automotive sector was the dominant consumer of lubricants in the African market, accounting for approximately 55% of total consumption. Between 2015 and 2019, lubricant usage in the automotive industry grew by approximately 8.6%. Moreover, COVID-19-related restrictions in 2020 resulted in reduced maintenance needs across various sectors. The heavy equipment industry saw the most significant decline, dropping by 5.05%, followed by a 4.7% decrease in the automotive sector.

PROBLEM STATEMENT

However, overtime, the continual usage of these oils leads to their chemical and physical characteristics undergoing degradation. This change can be due to heating when exposed to higher temperatures and exposure to oxygen, i.e., thermo-oxidation. LOs are stripped of their ability to carry out their main function, which is to protect the machine because of thermo-oxidation, consequently contributing negatively to the economic and ecological balance of a machine or engine. Degraded lubricating oil poses a numerous complications, which are the formation of sludge and varnish which will in turn reduce the efficiency of the oil hence a reduced performance of the automobile engine. It also leads to potential breakdown of an engine. In addition to the implications, engine emissions of volatile organic compounds (VOCs) from degraded oil pollute the atmospheric air, furthermore, disposing such oil will contaminate the soil and water killing aquatic life as well as damaging the fertility of the soil. For these precedent complications, resulting from the thermo-oxidation it is vital for the lubricating oil to function at minimal degradation and to find ways on how to improve its thermal and oxidative stability in a motor by analysing its degradation process. Therefore, the purpose of this project is proper understanding of the thermo-oxidation phenomenon by characterisation with evaluation of its kinematics. It also serves as a tool aimed at the reduce oil waste generation, and promote the responsible use of lubricants in various industrial applications which is vital in the sustainability of lubricant oils and automobile motors and may result in improved performance of an engine, longevity and its duration.

THE AIM

To investigate the thermal oxidative degradation of lubricating oils, focusing on the effects of temperature and oxygen exposure on oil stability hence clarify the underlying mechanisms of thermo-oxidation and suggest possible strategies to improve oil durability. This research contributes to the advancement of industrial maintenance practices to ensure continued reliability and performance of machinery in a variety of fields.

THE RESEARCH OBJECTIVES

- To understand thermo-oxidation mechanism as the primary process contributing to the degradation of lubricant oil
- To analyse the influence of temperature, oxygen and time in the degradation of lubricant oils through composition.
- To propose mathematical and kinetic models to help predict the evolution of thermo-oxidation, which will, help to improve the quality of lubricating oils and their behaviour hence contribute to mitigate the rate of thermo-oxidation.
- Evaluating the composition of additives in lubricant oils

CHAPTER I:LITERATURE REVIEW ON LOs

CHAPITRE I LITERATURE REVIEW ON LOs

This chapter provides a comprehensive review of lubricants, focusing on their composition, types, grades, and additive technology. The information presented here synthesizes insights gathered from a wide range of scholarly sources, including books, articles, and academic papers. The composition of lubricants forms the foundational aspect of their functionality, influencing their performance characteristics in diverse applications. Understanding the types of lubricants available such as mineral oils, synthetic lubricants, and blended, it also provides crucial information on their suitability for specific operating conditions and environments.

Moreover, lubricants are categorised into various grades based on viscosity, which is critical for maintaining optimal friction reduction and wear protection. The evolution of additive technology further enhances lubricant performance by addressing specific challenges like extreme temperatures, load-bearing capacity, and corrosion resistance

I.2 DEFINITION

Lubricant oils are derivatives of crude oil composed of a complex mixture of hydrocarbons [4]. Their common purpose in an automobile engine is to minimize the friction, heat and wear between mechanical components that are in contact with each other and to avoid corrosion, this leads to optimal functioning of an engine [5]

Figure I-1: Lubricating oil used on metal parts of an engine

[6]

The engine if the car rubs against each other to cause friction which consequently cause their wear, therefore lubricants are applied in motor engine parts as shown in **Figure 1-1**, with LO being applied between metal parts of an engine. Lubricating of the internal combustion engine is essential to reduce unwanted energy and material losses.[1][5]

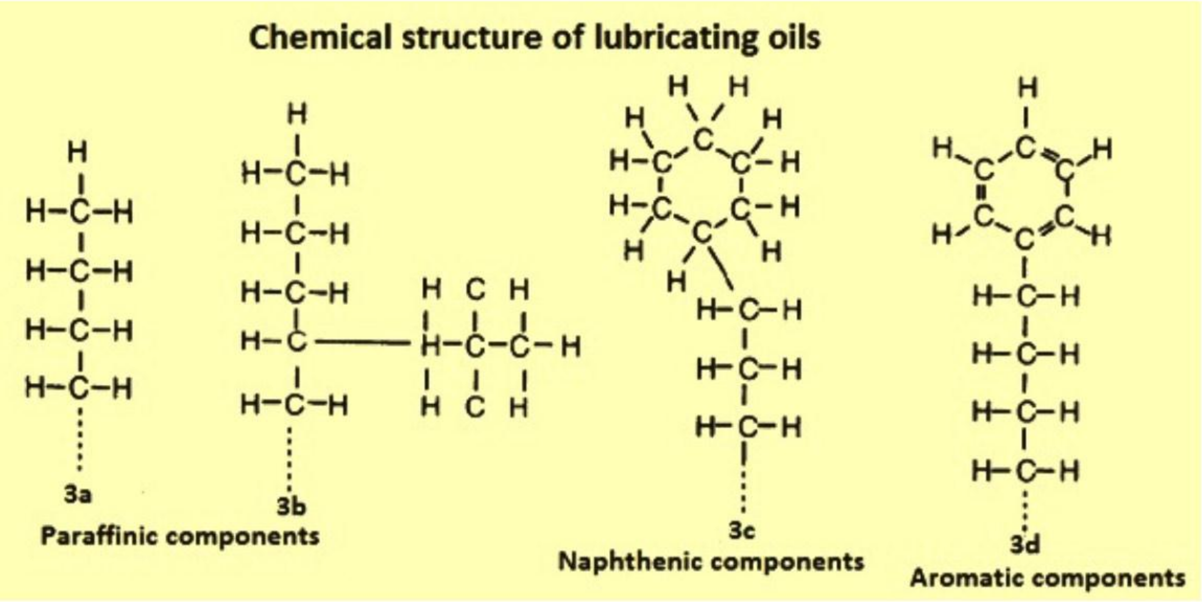
I.3 COMPOSITION OF LUBRICANT OILS

I.3.1 BASE OILS: They are composed of base oils/petroleum hydrocarbons (80-90%) [7]. These base oils may differ from one lubricating oil to another hence it is advisable for the manufacturer to accompany lubricating oils with technical sheets with information conveying their composition for safety purposes [8]. The main functional groups present in their base oils are naphtenes (cycloalkanes), aromatics and paraffins with carbon chains of 20 to 40 [9] represented in a clear structural form in figure I.2.

Parrafins: they are aliphatic hydrocarbons known for their good oxidative state and a low volatility.

Naphtenes: they are hydrocarbons that are cyclic, could be cycloalkane.

Aromatics: they are molecules with one or more benzene ring and a hydrocarbon chain.



Scheme I.1: The chemical structure of lubricating base oil [10]

I.3.1.1 BASE OIL GROUPS

The American Petroleum Institute (API) has classified base oils into five categories according to API 1509 as shown in Table 1. For lubricants to be obtained they undergo refining processes to eliminate by-products, it is through these processes where the initial base oil groups are derived from group I, II and III. Whereas, the Group IV base oils consist of fully synthetic for instance, polyalphaolefin oils. Any other oil not belonging to the aforementioned groups is attributed to group V. Lubricating oils typically start as one or more of these five API groups before the addition of any additives to the blend. Table one gives a detailed insights on their differences in terms of viscosity index, hydrocarbon percentage and sulphur content to make it easier to differentiate them.

GROUPE	VISCOSITY INDEX	SATURATED HYDROCARBON%	SULPHUR CONTENT%	DESCRIPTION
I	80-120	< 90	>0.03	- Low treated mineral oils - Paraffins or naphthenes - Suitable for less demanding applications
II	80-120	≥90	≤0.03	- More powerful mineral oils through hydrocracking - Pro: evaporation tendency, oxidation resistance, flash point -Contra: low temperature properties, pressure resistance
III	>120	≥90	≤0.03	- Very powerful mineral oils due to strong hydrocracking - High stability and uniformity of molecules - Almost synthetic purity
IV	-	-	-	-Chemically constructed polyalphaolefins (PAO) -High performance synthetic lubricants
V	-	-	-	-Includes all base oils that do not belong to the first four classes. -Used for the production of additives e.g. ester and polyester

Table 1: *Base oils groups and their descriptions* [11] [12]

I.3.2 ADDITIVES AND IMPURITIES (10-20%) : this percentage is mainly of additives, for the impurities their percentage is insignificant based on how well the lubricant oil was purified in the refinery [7].

I.4 TYPES OF LUBRICANT OILS

L0s are classified into four main types namely:

I.4.1 Synthetic oil: this oil is chemically engineered and synthesized from base stocks and additives. Synthetic motor oil undergoes a special chemical process. It has uniform-shaped molecules with fewer impurities and better properties compared to conventional oil. Generally, synthetic oil performs better in extreme high and low temperatures and contains higher-performing additives. However, it is very costly [12].

I.4.2. Conventional/ Mineral Motor Oil: Conventional motor oil comes in various viscosity grades and quality levels. It's suitable for engines with simple designs and for drivers with regular driving habits, rather than severe conditions. It is nonetheless very cheap to purchase and produce when compared to the other types. They are also free from acid when properly refines and have a less tendency to form emulsions with water. [13]

I.4.3. Blended Motor Oil: these are a combination of synthetic and mineral base oils, often mixed in varying proportions. Blended oils aim to leverage the advantages of both synthetic and mineral oils while mitigating their respective drawbacks. They may offer improved performance over conventional mineral oils at a lower cost compared to full synthetic oils. These oils are commonly used in automotive applications, providing a balance between performance, cost, and compatibility with existing lubrication systems [12] [14] [13]

I.4.4. High mileage: "specifically designed for cars with more than 75,000 miles. This type of oil can help reduce oil consumption, minimize leaks and oil seepage, and can also help reduce smoke and emissions in older engines" [15].

I.5 GRADES OF LUBRICATING OILS

.As previously mentioned, that conventional types can be graded, there is two grades existing, which are the monograde and the multigrade. The grades oils are named using the SAE (Society of Automotive Engineers).

I.5.1 Monograde oils:

- They have a single viscosity range hence the name mono, it can either be designed in a way that it works better in winter or better in warmer conditions. For instance those designed to work in warmer conditions are SAE-XW, the X is for the viscosity value and W for winter, e.g. SAE 10W, whereas those designed for warmer conditions are SAE-X, e.g. SAE2O.
- They are suitable for normal engine operating vehicles due to their inability to range viscosity with temperature change.
- Normally applied for racing cars or classical cars that require seasonal oil change.

I.5.2 Multigrade oils

- These Los have a variety of viscosity range hence the name multi denoting multiple grades. They are designed in ways suitable for both warm and cold temperature therefore their naming combines both of a single grade, for instance, SAE 20W10, this means their viscosity is 20 in cold temperatures simultaneously being 10 in cold temperature.

I.5.2.1 ADVANTAGES OF USING MULTIGRADE OILS OVER MONO GRADE OILS

- Versality: multigrade oils offer a balance between flowability at low temperatures and viscosity at high temperatures, making them suitable for a wide range of operating conditions and climates.
- Cold start protection: their rating of winter viscosity value rating ensures that the oil flows easily during cold starts, providing quick lubrication to critical engine components and reducing wear. Therefore, they have excellent cold-start performance due to low-temperature viscosity properties while the monograde oils have limited performance in extreme temperatures.
- High temperature protection: rating indicates that the oil maintains adequate viscosity at high temperatures, offering sufficient lubrication and protection under operating conditions. Even their performance is consistent across temperature extremes which is contrary with the monograde oils whose performance is only restricted to temperatures they are specifically designed for.
- Fuel saving: due to their better performance, good lubrication, the engine oil life time is a bit extended and may need changing less than those of monograde ones hence they are said to save fuel by 1.5 to 3%.
- Flexibility: they are ideal for year-round use as they can function better at any given extreme temperature unlike monograde oils.

To summarise this, multigrade oil offers optimal performance across a wide range of temperatures, ensuring consistency in viscosity levels regardless of temperature fluctuations. While most liquids become thinner as temperatures rise, multigrade oils maintain viscosity within a specific temperature range, providing versatility and reliability. In contrast, monograde oils lack specific viscosity characteristics at lower temperatures. Therefore, multi grade oils are designed in a way that they work better under any weather conditions [16] [17].

I.6 SEQUENCE GUIDE FOR OBTAINING LUBRICATING OILS

These oils are applied directly to surfaces in contact with each other to form a protective film, ensuring smooth operation and extending the lifespan of mechanical components, they are made up of certain-sized molecules, usually with 26 to 40 carbon atoms. These molecules need to be big and heavy to work well as lubricants. When crude oil is processed, the refinery sorts the molecules by size and weight and cleans them up to make various products. After crude oil is cleaned and partly turned into vapour by heating, it's separated in a tall tower. This tower separates the molecules based on how easily they turn into vapour, mainly because of their size.

Inside this tower, the hydrocarbons are turned into vapour and go up. As they rise, they cool down and turn back into liquid. This happens at different heights in the tower, mostly because of the size of the molecules [18].

The process of acquiring lubricating oils can be generalised into three main steps shown in scheme I.1:

SCHEME I.2: Major steps to summarising processes involved in obtaining lubricant oil.

I.6.1 EXTRACTION/EXPLORATION

I.4.1.1 Drilling: The process begins with locating potential oil reservoirs through geological surveys and exploration activities. Once a suitable site is identified, drilling rigs are set up to penetrate the Earth's surface and reach the oil-bearing rock formations. Various drilling techniques, such as rotary drilling or hydraulic fracturing, may be employed depending on the geological characteristics of the site [19]

I.4.1.2 Transportation: After drilling, methods such as pumping or natural pressure are used to extract crude oil from the reservoir and bring it to the surface. This crude oil is a mixture of hydrocarbons, along with impurities such as water, gas, and sediment. Surface equipment, including pumps, separators, and storage tanks, is used to process and store the extracted crude oil before it's transported to refineries for further processing [19]

I.6.2 REFINING

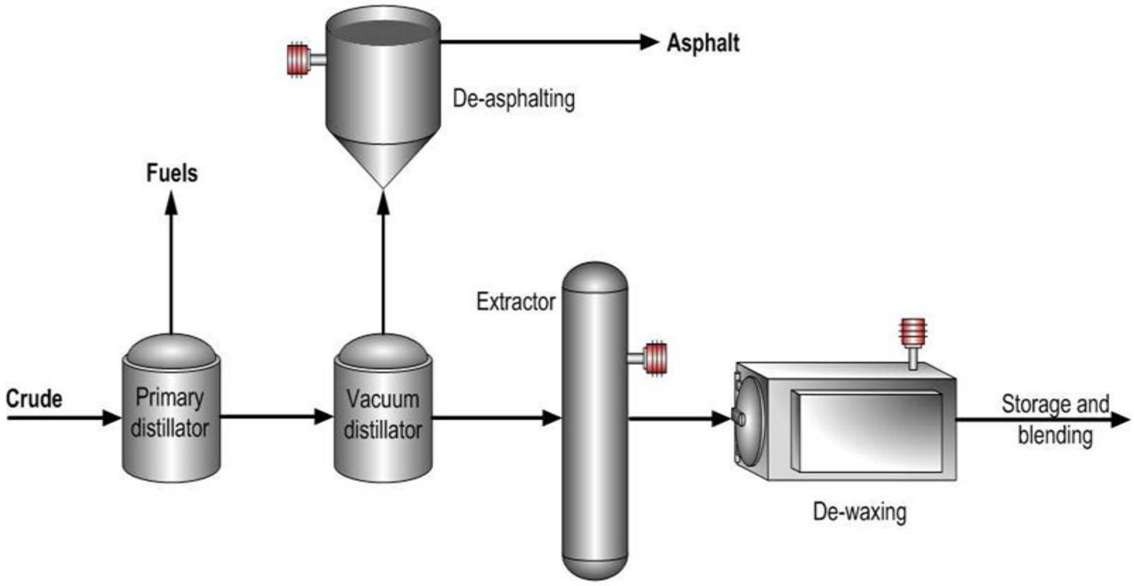


Figure I-2: Pictorial representation of refinery processes
[20]

I.6.2.1 Fractional Distillation*:*

This involves two steps of distillation as displayed in figure I.5 in the beginning of the refinery right after the crude oil send off the first reactors found are the two distillators: The primary distillatory involves fractional distillation where crude oil is separated into various fractions shown in figure I.6, based on differences in boiling points. This process is crucial for obtaining lubricating oils with the desired properties and characteristics.

During distillation, crude oil is heated in a furnace to temperatures ranging from 315 to 400 °C, causing it to vaporize. The vaporized crude oil is then fed into a distillation tower, also known as a fractionating column.

Inside the distillation tower, the vaporized crude oil rises through a series of trays or packing material. The tower is equipped with temperature controls, with higher temperatures at the bottom and lower temperatures at the top. As the vapour ascends the tower, it gradually cools down due to the decrease in temperature, leading to the condensation of the hydrocarbon vapours into liquid fractions at different levels within the tower.

The separation of crude oil into fractions occurs based on the boiling points of the various hydrocarbon components. Lighter hydrocarbons with lower boiling points, such as gases and naphtha, condense at the top of the tower and are drawn off as overhead products. Heavier fractions with higher boiling points, including lubricating oils, diesel, and residual fuel oil, condense at lower levels and are drawn off through side draw-offs or trays located at specific heights within the tower [21] [22]The lubricating oil will then be sent into the vacuum distillatory whose main purpose is to lower their boiling temperature.

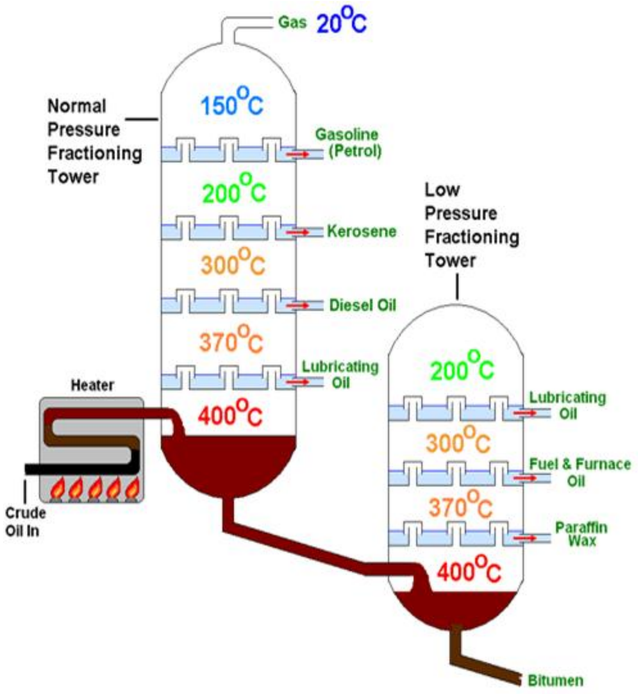


Figure I-3: Fractional distiller with a column distiller
[23]

I.6.2.2 Solvent Extraction

Solvent extraction refers to a method aimed at eliminating a significant portion of the aromatics and unwanted elements from oil distillates through liquid extraction. This process typically employs solvents like phenol, furfural, and sulphur dioxide that dissolves the aromatics and other impurities. After extraction, the resulting base stocks are known as raffinates, often called neutral oils. Additionally, the process yields an extract with a high aromatic content, which is highly valued and commonly used as a process oil or fuel oil [24].

I.6.2.3 Solvent dewaxing:

After using solvent extraction, the raffinates go through a process called dewaxing. This is done to make the oil flow better at low temperatures. Dewaxing separates the oil into two things: a leftover wax that's mostly made of paraffin, and a dewaxed oil that has paraffins, naphtenes, and a few aromatics. This dewaxed oil is used as the main ingredient in lots of lubricants [24].

I.6.2.4 Deasphalting:

This process involves separation of asphaltene compounds from heavy crude oil, the reason for this is that asphaltene compounds may cause complications later in the refining process such as deposition on refining equipment or catalyst deactivation, so it is advisable to remove them from the onset. These compounds are heavy oils that are insoluble in light hydrocarbons such as propane which is the most utilized, however butane can also be used, and these are heated at high temperature and pressure and cooled afterwards letting the heavy asphaltene to settle in a form of precipitate which is the separated from the solution by filtration. Now the filtrate is called deasphalted oil (DAO) [25].

I.6.3 TREATMENT:

I.4.3.1 HYDROPROCESSING: involves two process of hydrotreating and hydrocracking:

- Hydrotreating involves the addition of hydrogen to base oil under temperatures surpassing 315°C and pressures exceeding 3.4 GPa, facilitated by a catalyst. This method eliminates impurities, stabilizes the most reactive elements in the base oil, enhances its color, and prolongs its usability. However, hydrotreating alone is typically insufficient for complete base oil production.

- Hydro-cracking: represents a more rigorous version of hydrotreating. It involves passing the base oil feed over a catalyst bed with high activity, operating at temperatures above 325°C and pressures over 6.8 GPa. During hydrocracking, molecules in the feedstock undergo reshaping, with some being fragmented into smaller entities. The process effectively eliminates nearly all sulphur and nitrogen content while saturating numerous aromatic compounds with hydrogen. Molecular restructuring occurs as is-paraffins and saturated ring compounds are generated.

The second step is the formation of base oils discussed before as the major component in the composition of lubricating oil. Then the last step is corporating of additives to improve the quality of lubricating oils [26]

I.7 PHYSICAL AND CHEMICAL PROPERTIES OF LUBRICATING OIL

These qualities are tested for the evaluation of the quality of oil or how far it has degraded.

I.7.1 VISCOSITY

“Viscosity is technically defined as the fluid friction of an oil [27]. It is the resistance to flow; it is a pivotal characteristic ensuring effective lubrication of engine parts. The appropriate viscosity varies depending on the engine's design and operational circumstances. Higher viscosity oils are best suited for extreme conditions, while lower viscosity oils are preferred for everyday driving [28].

I.7.2 VISCOSITY INDEX

This is the variation of viscosity with temperature. When the viscosity index is high,they are able to maintain good performance regardless of the variations in temperature, they also ensure stable functionality under varying environmental conditions. [28]

I.7.3 POUR POINT

This refers to the lowest temperature in which the LOs can still flow or be poured hence the name, it is at this temperature where oils start to solidify. When paraffins Los solidifies, they crystallise and crosslink. This causes the oil to appear milky and cloudy. As a result, the viscosity of the oil rises until it transforms into a solid, waxy substance. Once solidified, the oil loses its lubricating abilities because it can no longer effectively reach and distribute across lubrication points.

I.7.4 FLASH POINT

This is the lowest temperature at which oil releases flammable vapours. Oils with higher flash points help reduce the risk of engine combustion, thus ensuring operational safety and stability. It is important to know this temperature as it is the lowest temperature indicating the risk in which fire ignition of the oil is likely to occur. Fuel that ignites easily due to having a low flash point can cause problems with how the engine runs and may even lead to safety issues [29].

I.7.5 OXIDATION STABILITY

It is the ability of lubricants to resist chemical reactions with oxygen over time, which can lead to degradation and the formation of harmful by-products such as acids, sludge, and varnish. A lubricating oil with high oxidation stability maintains its effectiveness and prolongs its service life, ensuring proper lubrication and protection of engine component [30].

I.7.6 THERMAL STABILITY

The thermal stability of a fluid refers to its capacity to withstand decomposition due to temperature alone. This characteristic sets the uppermost temperature threshold for a tribological system fluid that will ensure continual unimpaired service. The most significant change in fluid properties caused by thermal decomposition of organic molecules is an increase in vapour pressure caused by the shearing of molecules into smaller, more volatile fragments [31].

I.7.7 DENSITY

Density is described as the mass per unit volume of the oil. It is a crucial parameter that affects various aspects of lubricant performance, including its flow behaviour, thermal conductivity, and lubricating film thickness. [13]

I.7.8 REFRACTIVE INDEX

It is a measure of how much the speed of light is reduced as it passes through the oil. It is influenced by factors such as the oil's composition and purity. The refractive index can provide insights into the oil's quality and composition, which can be useful for quality control and analysis purposes in lubricant manufacturing and usage. [32]

I.8 ADDITIVE TECHNOLOGY

In order to enhance the quality and performance of lubricant oils and their properties, it is essential to blend in additives in their production. Below are some of the additives that aid in the efficiency of LOs and their uses together with how they carry out their aid function.

I.8.1 Friction modifiers (FM): They help to reduce friction, making the engine smoother and more efficient. They are composed of a hydrocarbon chain and a polar head group (amine, amide or carboxylic group).

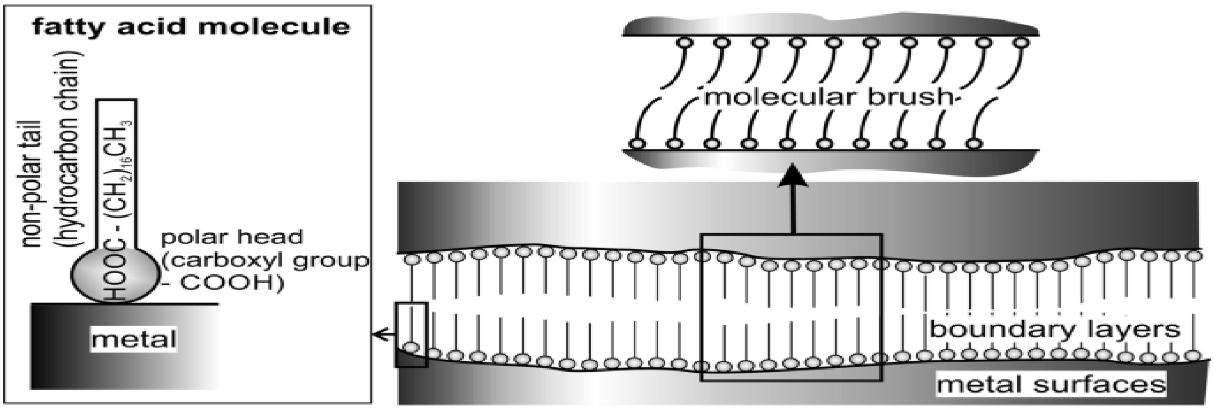


Figure I-4: Chemical structure of friction modifiers

[33]

MODE OF ACTION: it is absorbed in the metal during lubrication, with the polar labelled in figure head attaching itself to the metal parts that are in contact with each other while the hydrocarbon remains solubilised in the lubricant film and help them (metal part in contact) to slide past each other with ease.

Example:

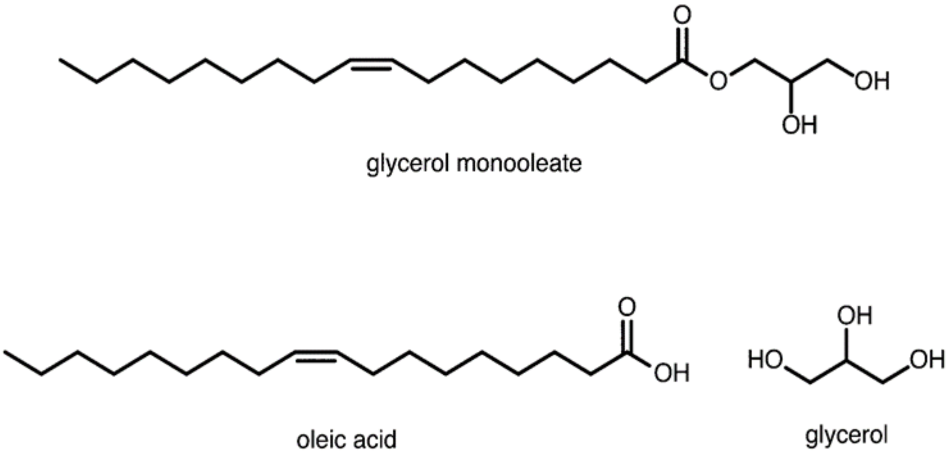


Figure I-5: Chemical structure of glycerol Mono-Oleate

[34]

I.8.2 Corrosion inhibitors:

They protect metal surfaces from corrosion or rusting, like FM they have a polar head and a hydrocarbon chain.

Example:

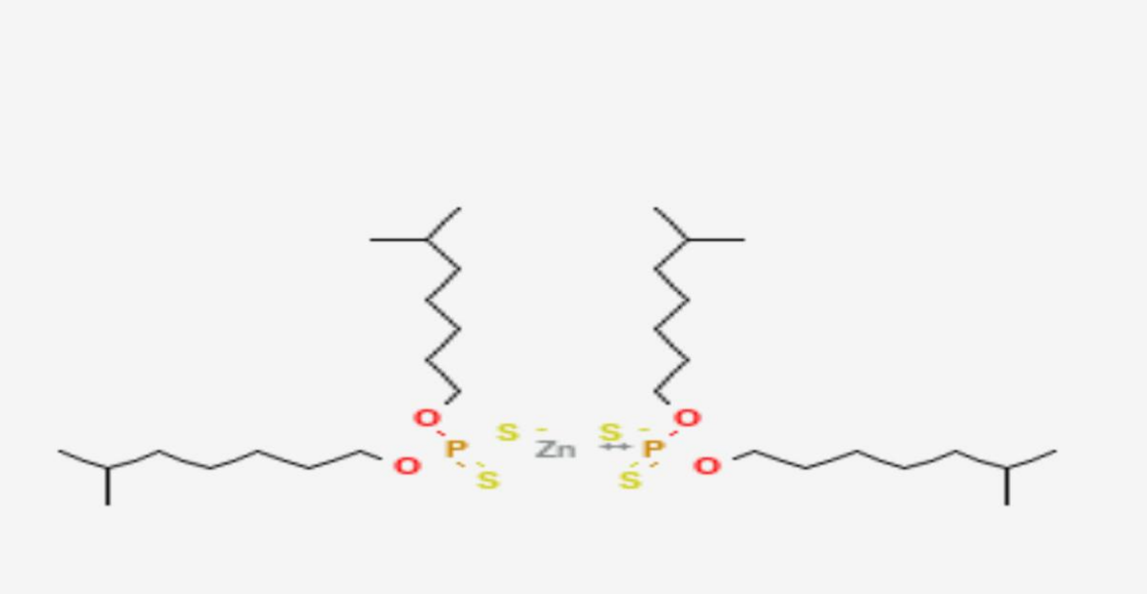


Figure I.6: Chemical structure of Zinc diisooctyl dithiophosphate (ZDDP) [35]

They also attach the polar head to the metal surface with the hydrocarbon chain solubilised in the lubricating oil, they prevent corrosion by forming a cohesive, continuous film that prevent water from reaching the metal surface. Figure I.10 is a pictorial demonstration of how they carry out their function.

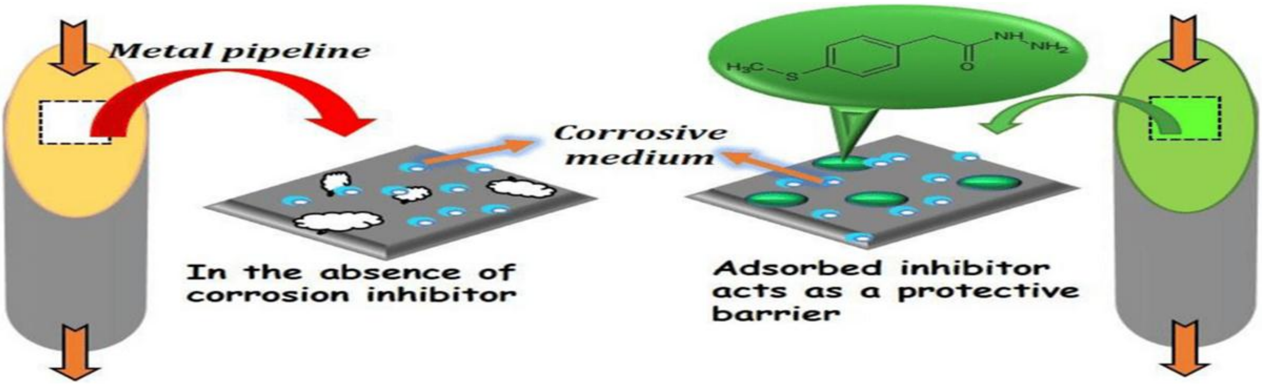


Figure I.7: corrosion inhibitors improving the corrosion resistance of LOs [36]

I.8.3 Viscosity index improvers:

They allow the fluid to flow more freely either at a lower/higher temperature so it can reach the bearings quicker. They are high-molecular-weight polymers that exhibit unique rheological properties. These polymers are soluble in the lubricating oil and can undergo conformational changes in response to temperature variations. At low temperatures, the polymer chains are coiled or compact, contributing minimally to viscosity. As temperature increases, the polymer chains expand or uncoil, increasing their contribution to viscosity.

I.8.4 Anti-oxidant:

They assist by improving the resistance of LOs from oxidation which is a process promoting the thermo-oxidation, hence the degradation of lubricants. Therefore their function is to enhance the oxidative stability of lubricating oils. They consist of hindered phenol, amines natural acids and pyrazines

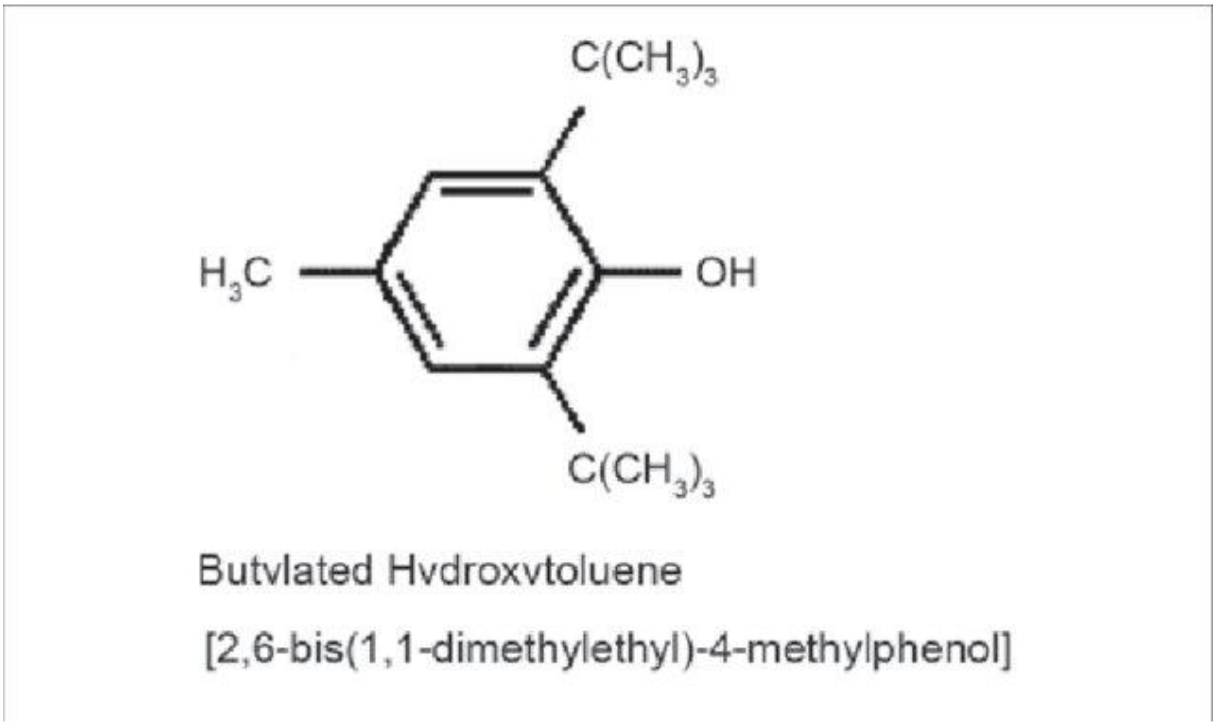


Figure I.8: Chemical structure of Butylated hydroxytoluene [37]

MODE OF ACTION:

The hindered phenol intercepts the formation of free or peroxy radicals, which encourage the oxidation, therefore they join with them to form a hindered radical, which discourages oxidation as demonstrated in equation (1) where the anti-oxidant reacts with the peroxy radical.

ROO’+ AH → ROOH + A’……………………………………………………Equation(1)

Where:

ROO’: Free/ peroxy radical

AH: Anti-Oxidant

ROOH: Hydro-peroxide

A’: Anti-Oxidant radical

More additives exist such as:

- Anti-freeze: They help adapt the various engine oils to their environment by modifying the oil’s hardening temperature.
- Detergents: prevent the formation of deposits and also neutralize any acidic substances present in the LOs.
- Anti-foaming agents: They minimise the formation of foam which is promoted by the use of detergents and reduces the efficiency of the LOs.

CHAPTER II: OVERVIEW OF THERMO-OXIDATION

CHAPITRE II OVERVIEW OF THERMO-OXIDATION

This chapter delves into the reviews of thermo-oxidation of LOs, it incorporates the mechanisms of Thermal Degradation: Examining oxidation, polymerization, and hydrolysis processes that alter viscosity and acidity, leading to the formation of varnishes and sludge. Kinetics of Degradation: Studying the rates and pathways of degradation over time and under different temperature conditions, using kinetic models to predict these processes. Application of Thermodynamic Laws: Applying basic principles to quantify energy changes and reaction rates during degradation events. We discuss the tools for oil analysis discussing methods like thermogravimetry analysis and Fourier-transform infrared analysis for detecting and analysing degradation products.

Furthermore, we review background studies of works which have already investigated on a similar topic. Drawing from studies by E. B. Beran et al. (2008) on thermo-oxidative effects, Santos et al. (2015) on thermodynamic parameters using thermogravimetry, M.A.K. Diaby et al. (2009) on kinetic modelling, and G. C. Ofunne et al. (1990) on oxidation stabilities, this chapter aims to provide a clear understanding of how thermal degradation impacts lubricant oils. It sets the stage for developing strategies to improve lubricant performance and reliability in various industrial and automotive settings.

II.2 DEFINITION

Thermo-oxidation oil is described as the chemical reaction that occurs when lubricating oil is exposed to high temperatures and oxygen typically in the process of metals (these metals favour thermo-oxidation by acting as catalyst.[23][31]

II.3 FACTORS INFLUENCING THERMO-OXIDATION

- Oxygen: it is a main component in almost all chemical reactions (which will be discussed later) that occur during thermo-oxidation, it oxidises the hydrocarbons in lubricant oils, acts as a catalyst speeding up the hydrolysis reactions. It is just always present initiating and encouraging thermo-oxidation.
- Temperature: as the term goes, “thermos” which is temperature, therefore it takes elevated temperatures to degrade the oil, it affects its viscosity, it becomes less viscous

hence unable to carry out its function of lubricating the engine well. Studies have indicated that elevated temperatures catalyse cracking, oxidation, and polymerization reactions, as well as enhance the desorption of lubricants, which can have a detrimental effect on directional adsorption, cause the oil film to melt, and decrease anti-foaming performance.[38]

- Time: The primary factor leading to engine oil oxidation is the temperature at which it ages, with aging time being the subsequent influential factor. Time is directly proportional to the degradation of oil, the more time oil is exposed to oxygen and temperature the more it degrades.[39]
- Catalysts: they alter the rate of thermo-oxidation therefore speeding up the reactions, they could come in the form of chemical molecules such as oxygen, or even the physical metals act as catalyst in the oxidation process.
- Friction: when metal parts in an automotive engine rub against each other, they produce heat, thus as aforementioned, it is the increase in temperatures that favours thermo-oxidation.

II.4 CHEMICAL REACTIONS PROMOTING THERMO-OXIDATION OF AUTOMOTIVE ENGINES

II.4.1 OXIDATION:

The hydrocarbons in lubricating oils are oxidised and the carbon bonded to the oxygen is replaced by oxygen forming carbon dioxide, water and carboxylic acids. This affects the colour, viscosity and Total Acid Number (TAN) of the LO hence reduce its efficiency. Moreover, intermediates such as hydrogen peroxide may be formed during oxidation, these intermediates can further react to form polymers. It also leads to the formation of low weigh materials such as aldehydes, ketones, acids and alcohol. There are three stages in the oxidation process, the first one being: the reduction in the levels of antioxidants and anti-wear additives, succeeded by the oxidative breakdown of the base oil. Throughout this phase, there is accumulation of polar organic compounds within the oil, including ketones, alcohols, carboxylic acids, and esters. The last one is polymerisation which will be discussed in detail later in this project.

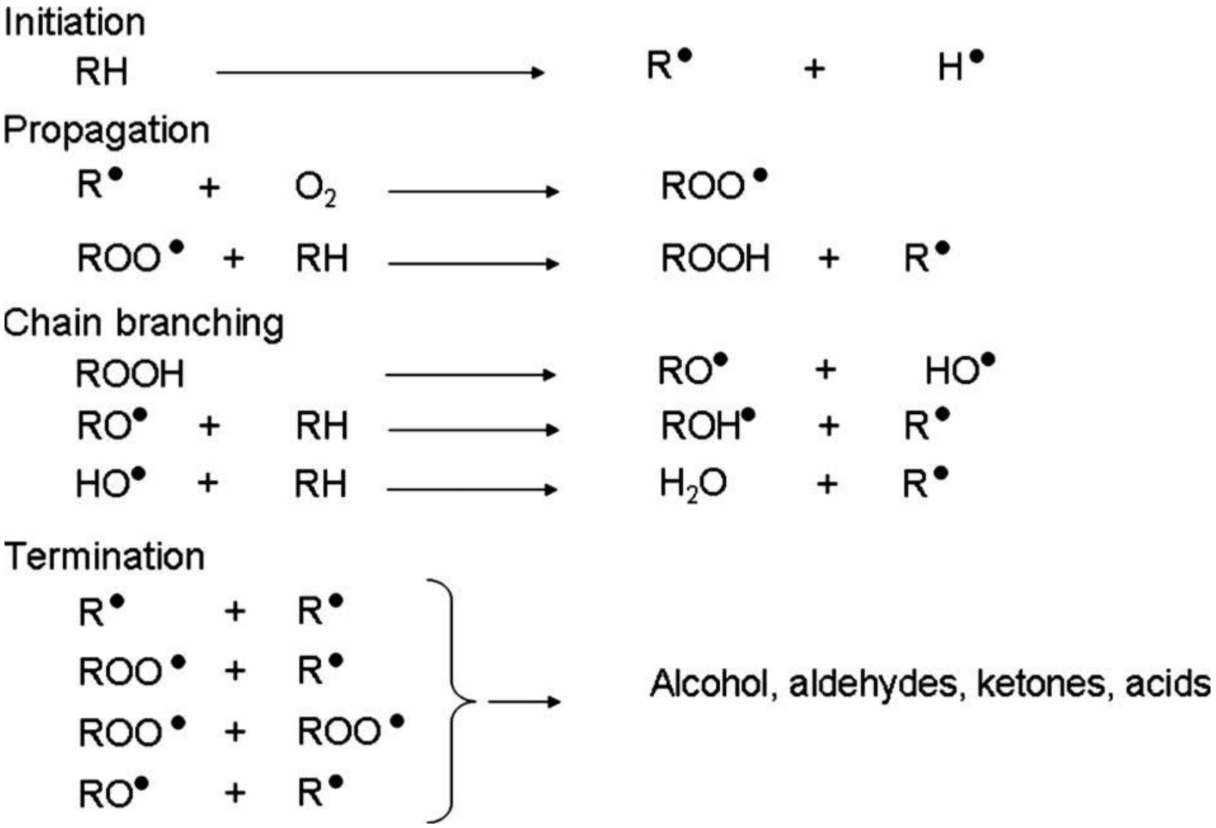


Figure II.1: Mechanism of oxidation in the formation of low weight molecules.[40]

Figure II.1 summarises the formation of low molecular weight, where in the initiation, there is break down of molecules present in the LO due to the heat or high temperatures, this causes them to be unpaired and highly reactive. Then oxygen present in air reacts with the unpaired radicals forming peroxy molecules. As previously mentioned, LOs are hydrocarbons molecules, therefore the hydrocarbon will react with the peroxy molecule to for hydro peroxide, these are high unstable and would decompose into free more radicals. The free radicals further undergo crosslinking reactions to form low weight molecules. [30][41][42]

The kinetics of thermo-oxidation is governed by Arrhenius equation**,**

$$\mathbf{k = A\ exp\ (\frac{-Ea}{RT})}$$ **……………………………………………………Equation (2)**

Where: A represents a constant, Ea stands for the activation energy required for a reaction per mole of energy, R denotes the molar gas constant, and T represents the temperature in K.Lastly K the rate of reaction constant. With every 10°C rise in temperature, the oxidation rate will double. The oxidation process consists of multiple steps, each contributing differently to the degradation of oil. Hydrocarbon chains react with oxygen to produce corrosive carboxylic acids. These acids undergo cleavage to generate highly active radicals, which then engage in reactions with other hydrocarbons, promptly leading to the formation of either another radical or a carboxylic acid. The radical reaction follows a cyclic pattern and necessitates deceleration by antioxidants. The presence of metals, both as wear debris and surface metals, accelerates these process. [30]

II.4.2 POLIMERISATION:

The oxidation products now further undergo other reactions to form high molecular weight compounds, with the unsaturated hydrocarbon molecules undergoing cross-linking reactions in the presence of oxygen, leading to the formation of polymers. These may cause the formation of sludge and vanish (dirt) in the lubricating oil. The products of polymerisation increases the viscosity of lubricating oils making it harder for it to flow hence it cannot carry out its function efficiently. This will lead to low performance of oils

II.4.3 HYDROLYSIS:

Lubricant oils are hygroscopic in nature that means it absorbs water from the environment, which is the main reactant in the hydrolysis reaction. In the process of hydrolysis which is the degradation of base oil molecules by formation of acids, oxygen acts as a catalyst speeding up this reaction. This will affect the chemical structure, the colour or the viscosity of lubricant oils hence their efficiency therefore leads to rusting of machine and corrosion. Base oils of the ester type are particularly vulnerable to hydrolysis. The chemical bonds they contain, called ester linkages, make them highly susceptible to hydrolysis, which can cause these bonds to break apart. The hydrolysis involves several steps, of which the slowest is the formation of a covalent bond between the oxygen atom of the water molecule and the carbon atom of the ester. In succeeding steps, which are very rapid, the carbon–oxygen bond of the ester breaks and hydrogen ions become detached from the original water molecule and attached to the nascent alcohol molecule. The whole reaction is represented by the equation 2 below:

$$\mathbf{CO{-}OR' + H2O \rightarrow RCO{-}OH + R'{-}OH} \text{......................} \mathbf{Equation\ (3)}$$

In which, RCO—OH denotes a molecule of a carboxylic acid, R′—OH denotes a molecule of an alcohol..The products of hydrolysis for instance alcohol and carboxylic acids can act as catalysts in thermo-oxidation of lubricant oils. [42][43]

II.4.4 NITRATION AND SULPHATION

The presence of sulphur may lead to the formation of SOx, organic sulphones and sulphoxides via oxidation, and sulphurous acid esters when SOx reacts with organic compounds present in oil. Engine oils can also react with nitrogen oxide, resulting in additive depletion, increased viscosity and deposit formation. Sulphating occurs when sulphur compounds are oxidised and results in increased varnish and sludge. Similarly, when heat is present, the air's nitrogen and oxygen react to create nitrous oxides (NO_X). These oxides can mix with engine oil, leading to its premature thickening. This occurs due to issues such as incomplete exhaust cleaning, improper fuel-to-air ratio, low engine temperature, or leaks in piston seals. [44][45]

II.4.5 DECOMPOSITION

The presence of oxygen may induce the additives added to the LOs to decompose, this may affect its overall stability as well as its performance. For example: decomposition of calcium carbonate ($CaCO_3$) to form calcium oxide (CaO) and carbon dioxide (CO_2).

$$\mathbf{CaCO_3 \rightarrow CaO + CO_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ Equation (4)}}$$

This calcium carbonate is result of excess detergents or rust inhibitors (additives containing calcium sulphonate), which help to improve the quality of oils however their excess can form calcium carbonate. It is good in that it can be used as green lubricant that can also be used as an additive however it causes problems if not managed properly of filter clogging. A clogged fuel filter can deplete the fuel supply going to the engine and cause problems with stalling in severe cases. It also decomposes to form carbon dioxide which is dissolved in the lubricating oil to form carbonic acids that increases TAN, this acid corrodes the engines.

II.5 STUDY OF THERMO-OXIDATION

To detect or analyse the extent to which LOs have degraded through thermo-oxidation, scientists use simulation and accelerated ageing of oil while characterising with conventional experiments and these are divided into classical and technical experimental methods.

II.5.2 TECHNICAL METHODS

PROPERTY	INSTRUMENT	DETAILS
➢ VISCOSITY ➢ VISCOSITY INDEX (ASTM D445, D2983)	- Viscometer (Ubbelohde) for kinematic viscosity -For dynamic Rheometers are used	It measures the ability of lubricating oil to flow in Pascal's, from the data collected on viscosity, viscosity index can also be derived.
➢ DENSITY (ASTM D941)	-Density meter -Pycnometer	It provides data about LOs' mass and volume and can therefore derive the mass per unit volume, which is important for quality control and determining concentration.
➢ REFRACTIVE INDEX (ASTM D1747)	-Abe refractometer	From the refractive index we able to deduce the quality, composition and purity of Los depending on how fast light travels through them, change in their refractive index denotes that there is contamination.
➢ Pour point (ASTM D97)	-Pour point tester/apparatus	It gives information about the ability of the lubricant oil to be efficient in cold temperatures.
➢ FLASH POINT	-Flash point tester apparatus	It provides information on the flammability of the oil thus help to know the conditions to store or handle it in to avoid hazards.

IV.4.1 CLASSICAL METHOD **Table 2:** Classical analyses and their significance [40][46]

- FOURIER TRANSFORM INFRARED ANALYSIS

This is used to analyse qualitatively the functional groups as allocated in **figure II.2 below**, for absorbed or transmitted red light when it passed through oil samples, it also gives insightful information molecular structures, and chemical bonds present in our lubricant oils. Therefore, it can be used to detect any changes in functional groups to show degradation [47]. Furthermore, it quantitatively can be used to analyse the carbonyl index, hydroxyl index as well as predicting the activation energy using **Equation 3.** These parameters are crucial in the study of oils as they denote the extent of degradation [1][43]

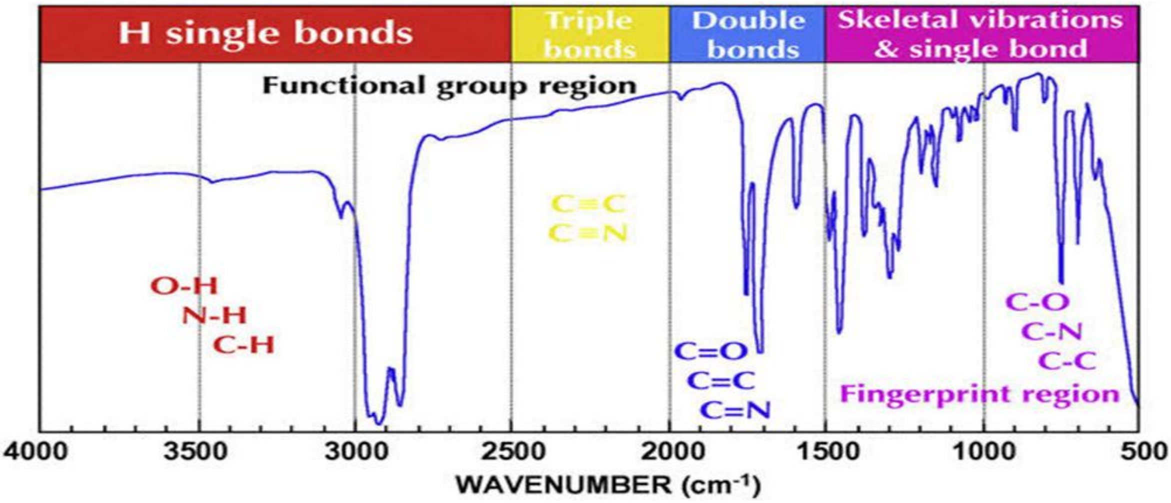


Figure II.2: Pictorial representation of the identification of bands in a transmission analyses of FTIR [48]

- TOTAL ACID NUMBER (TAN) ASTM D664

It quantifies the amount of acid contained in the oil therefore can monitor increase of decrease overtime when the oil is being degraded. [49] This involves dissolving the sample in toluene and isopropanol with a bit of water and titrating that solution with alcoholic potassium hydroxide.

- GAS CHROMATOGRAPHY/MASS SPECTROMETRY(GC/MS)

They work hand in hand with two analytical methodologies to identify and quantify the presence and concentration of chemicals found in LOs. Gas chromatography (GC) separates volatile components in a mixture by vaporizing a liquid sample and transporting it through a coated column via a carrier gas. The compounds interact with the stationary phase, resulting in differential retention times. The separated compounds are then analysed by a mass spectrometer (MS), which identifies and quantifies them based on their mass, providing insight into their structural and chemical properties.

- THERMOGRAVIMETRIC ANALYSIS(TGA) ANALYSIS

  It analyses the thermal stability of lubricant oil hence can detect the extent of which the oil has degraded by monitoring its stability over time with characterisation. In this technique the mass of the lubricant oil is monitored as a function of temperature. These instruments can measure various factors such as water loss, solvent loss, plasticizer loss, decarboxylation, pyrolysis, oxidation, decomposition, filler content by weight and ash content by weight. Typically, these measurements are conducted during heating processes, although some experiments may yield data during cooling as well. There exists two instruments. [31][43]

- NUCLEAR MAGNETIC RESONANCE (NMR) ANALYSIS

  NMR spectroscopy uses the magnetic properties of atomic nuclei to give a clearer insight into the molecular structure, composition, and dynamics of compounds. With this technique, various components within lubricating oils, including hydrocarbons, additives, contaminants, and degradation products, can be identified and quantified. Additionally, NMR spectroscopy contributes in the characterization of additives present in lubricating oils, offering valuable information about their chemical structure, concentration, and distribution within the oil. Furthermore, it plays a crucial role in quality control efforts, ensuring that lubricating oils meet industry standards and regulatory requirements. By monitoring changes in NMR spectra over time, we can detect and track the degradation of lubricating oils due to factors such as oxidation, thermal decomposition, and contamination.[50][51][52]

- UV VISIBLE ANALYSIS

  It is used to assess the chemical composition of lubricating oils, information such as the contaminants of thermos oxidation by products can be detected over time if the spectrum has additional chemicals it is shown. The spectrum gives information on the intensity of absorbed or emitted radiation of frequency or wavelength.

The law of Lambert-Beer describes the relationship between the absorbance of light by a solution and the concentration of the absorbing species in the solution. The law states that:

$A= -\log= \varepsilon l C$……………………………………………………………Equation4

Where: A is the absorbance of the solution, ε is the molar absorptivity and l is the path length of the sample cell and C is the concentration of the absorbing species in the solution.

The validity of Beer-Lambert's law:

- Applies for monochromatic radiations
- Applies for solutions sufficiently diluted so that they cannot modify the properties of the sample.[53][54]

II.5.1 EFFECTS OF THERMOOXIDATION

The thermo-oxidation degradation on lubricant oils directly affects the LOs and indirectly affect the engine through the degraded oil.

- Viscosity Increase: Thermo-oxidation can cause the formation of oxidation products such as acids, aldehydes, and peroxides, which can increase the viscosity of the oil. This increase in viscosity can impair lubrication efficiency and lead to increased friction and wear.
- Formation of Deposits: Oxidation products and degradation by-products can form insoluble deposits and sludge in the oil, which can clog oil passages, filters, and other lubrication system components. These deposits can interfere with proper lubricant flow and heat dissipation, leading to reduced efficiency and increased risk of component failure.

- Acid Formation: Thermo-oxidation can result in the formation of acidic compounds in the oil, such as carboxylic acids. These acids can accelerate corrosion of metal surfaces in the lubrication system, leading to increased wear and potential damage to components.

- Base Oil Degradation: Thermo-oxidation can degrade the base oil molecules, leading to a reduction in the oil's lubricating properties and thermal stability. This degradation can result in decreased oil life and increased frequency of oil changes required to maintain lubrication system performance.
- Increase in Oxidation Stability: In some cases, exposure to controlled levels of thermo-oxidation can actually improve the oxidation stability of lubricating oils by promoting the formation of stable oxidation products and enhancing the oil's resistance to further degradation. However, prolonged exposure to high temperatures and oxygen levels will ultimately lead to detrimental effects. [42]

Ultimately the degraded oil will fail to serve its purpose efficiently resulting in reduced lubrication, increased wear, reduced performance, this will lead to engine breakdown, reduced performance and durability.

II.6 BACKGROUNG STUDY

This research serves as a continuation on the already ongoing investigation and studies that have been undertaken to analyse and examine the effects of thermal degradation on lubricant oils. In the research of E. B. Beran et al(2008**)**, they investigated the influence of thermo-oxidative degradation on the biodegradability of lubricant base oils by using 4 different types and characterising before thermal degradation and after using the viscosity at (40°C and 100 °C) and acid number for 6hours each heated 150°C. Their research revealed that thermo-oxidative degradation indeed caused alterations in both the chemical and physical properties of the base oils, as evidenced by an increase in viscosity and acid number. Despite these changes, the biodegradability of the oils remained unaffected. Consequently, the researchers concluded that thermo-oxidation does not significantly impact the biodegradability of lubricant oil. As a researcher, this study is beneficial in terms of providing more insightful information concerning thermal degradation and help me to achieve the number one objective if understanding deeply the mechanism of thermo-oxidation of lubricant oils. Moreover, it offers more knowledge on the toxicity and the role played by the base oils in contributing to environmental pollution. [55]

Santos et al (2015) undertook another research on the thermal degradation, where they investigated the thermodynamic and kinetic parameters on thermal degradation of automotive mineral lubricant oils determined using thermogravimetry. The research investigated the thermal degradation of automotive mineral lubricant oils, specifically focusing on a SJ group oil with SAE viscosity grade 40 W. Using thermogravimetry, they studied the thermodynamic and kinetic parameters of degradation over time intervals from 1 to 48 hours at various temperatures. Non-isothermal analyses under different atmospheres and heating rates were also conducted. Results indicated that higher degradation temperatures lowered onset decomposition temperatures, reducing sample stability. Significant mass loss was observed at 190°C for 48 hours, forming polymeric compounds, while mass loss decreased at 210°C due to gum and precipitate formation. The study contributes insights into enhancing lubricant oil efficiency under thermal stress but has limitations in scope, focusing solely on a specific oil type with a limited suitability for year-round use in all weather conditions. [56]

In addition, M.A.K. Diaby et al (2009) investigated the kinetic study of the thermo-oxidative degradation of squalene C30H62 modelling the base oil of engine oil. Squalane was chosen due to its similar physical and chemical properties as the lubricant oil of base group III of the lubricant SAE 5W30. The thermo-oxidative degradation of this hydrocarbon was carried out under atmospheric pressure conditions using a tubular furnace. The temperature varied from 180°C to 205°C and the duration of the tests were varied from 6hrs to 72 hrs to determine an oxidation reaction rate equation. Consequently, the impact of both antioxidants on the oxidation rate equation was examined using advanced analytical experiments such as the FTIR spectroscopy, GC/MS, these analytical tests allowed them to use the kinetic models hence estimate kinetic behaviour of the Squalane. In conclusion, data analysis allowed formulating a kinetic model, which can be used as a practical analytical tool to follow the effectiveness of thermal oxidative degradation of squalane without antioxidants. This kinetic model can be easily generalized at different temperatures. Nevertheless, in the presence of antioxidants, application of the kinetic model requires first the determination of the observed threshold temperature for the antioxidants investigated. The study proposed a comprehensive kinetic model describing the oxidation pathways which was specified still needs confirmation by other researchers to be validated.[43]

Lastly, G. C. Ofunne et al. (1990) conducted a study on the high-temperature oxidation stabilities of two grades of automotive crankcase oils and their base oils under conditions that simulate those encountered in the internal combustion engines. They employed several bench simulation tests which involved leaving the oil SAE-40 monograde and SAE 20W50 multigrade at a temperature of 180°C for 65 hours at an air flow of 1L/min. Through laboratory tests, they evaluated the effects of operating conditions on oil degradation. Their findings underscored relationship between temperature and degradation rate, with oxygen concentration. Their findings revealed significant increases in oil viscosity, formation of varnish and sludge deposits, and elevated acidity levels following extended engine operation. These degradation-induced effects were shown to impair engine lubrication, increase friction, and accelerate wear, highlighting the critical importance of mitigating oil degradation for ensuring engine reliability and efficiency.[57]

While each study uniquely and collectively provided a comprehensive evaluations that chemical and physical changes during thermal degradation, a more detailed examination of the ecological footprint of degraded lubricants, including the fate of degradation by-products in the environment, would be beneficial. Also, the precedent literatures concentrate on particular types or components of lubricant oils, such as mineral oils or specific viscosity grades. However, there is a call for research that encompasses a broader spectrum of lubricant formulations used in various industries and applications

CHAPTER III:EXPERIMENTAL DESIGN,DISCUSSION AND RESULTS

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III.1 PART I EXPERIMENTAL PROCEDURES

The first step in the experimental part is to characterise the waste oil collected from the mechanic, which was changed after 3 months, 3900 km and virgin oil so that we can use them as reference to monitor changes in the composition and other physico-chemical properties of the oil. Then the next step would be to simulate different samples of lubricant oil in the oven as our engine model then characterize the oil. This chapter encompasses the procedures and methodologies on how I carried out the experiments in the laboratory as well as the results given with their analysis and interpretation.

III.1.1 TRACEABILITY OF THE WASTED AND VIRGION OIL

Both are :

- TOTAL QUARTZ 7000s of SAE 10w40, (80% base oils and 20% additives)
- Synthetic based engine oil
- Silver (mid-tier range)
- API SN/CF
- Approved by PSA B71 2300 (backward compatible PSA B712294), VW 501.01/505.00, Renault RN 0700/07105

For wasted oil, the oil collected at the mechanic in Bejaia town, where it was changed after 3 months after travelling 3900km.

Key functions

- Protect mechanical
- Reduce friction
- Evacuate dirt
- Contribute to sealing of the engine
- Reduce fuel consumption

Customers benefits

- Manufacturers Standards: TOTAL QUARTZ 7000 10W-40 satisfies rigorous manufacturers’ standards (see above), while guaranteeing perfect and constant quality.

- Resistance to Oxidation: Thanks to the good quality of its base oils and additives, TOTAL QUARTZ 7000 10W-40 provides a specific resistance to oxidation.
- Engine protection and cleanliness: This oil ensures good engine cleanliness, reducing particle accumulation in the motor via efficient dispersant power.
- Long-term wear Protection: Long-term wear protection of engine parts (distribution, ring, plunger and liner) increasing engine life.

CHARACTERISTICS[2]

TEST	UNIT	TEST METHOD	RESULT
Viscosity grade	-	SAE J300	10W-40
Kinematic viscosity at 40°C	mm^2/s	ASTM D445	96.8
Kinematic viscosity at 100°C	mm^2/s	ASTM D445	14.81
Density at 15°C	kg/m^3	ASTM D1298	873.6
Viscosity index	-	ASTM D2270	160
Pour point	°C	ASTM D97	-24
OC Flash point	°C	ASTM D92	232

[2] The characteristics given above are obtained with a standard tolerance threshold during production and may not be considered specifications.

TECHICHAL SHEET EXTRACTED FROM TOTAL ONLINE SITE: [58]

III.1.2 SIMULATION

We used 18 test tubes, labelled them each according to the time interval taken to take it out of the oven, the time intervals were 6hrs,12hrs, 24hrs,36hrs,48hrs and 60 hrs, for each time interval we had 3test tubes. We weighed them then poured in each one of them 20ml of lubricating oil then weighed again to get the mass of each lubricant oil. Then they were all sealed immediately to avoid contact with air, which can lead to oxidation. The oven was put at a constant temperature of 150°C and the back was left open to allow air to circulate uniformly in the oven then our test tubes were introduced and the sealing was taken off then we started counting time. At each intervals, three test tubes were removed immediately and weighed with precise digital analytical balance, this was to monitor the mass evolution of degraded oil at different time intervals.

Figure III.1: Precise analytical digital balance .

Figure III.2 (a) & (b): Binder oven front . and back side

[46] [47][59][60]

III.1.3 REFRACTIVE INDEX (ASTM D1747) [61]

- Description of the Equipment

With the refractometer, there are two prisms: a mobile prism, also known as the illumination prism, and a fixed prism, referred to as the reference prism. The device includes two eyepieces: one for adjusting the separation between the illuminated and dark zones and the other for reading the index scale. Both eyepieces are equipped with a lens system for clear vision. Additionally, there is a lighting device for the index scale, which consists of a small circular flap with a mirror. To adjust the separation limit, there's a knurled button positioned for the bottom eyepiece's reticule. Another knurled button is available to rotate the compensating prism, aimed at eliminating any colorations that may arise in the separation limit between the light and dark zones.

Figure III.3: Refractometer of Abbe

- Conditions of operating

This index is measured using a refractometer. It is linked to temperature and is measured at 20˚C for oils therefore noted as n20 meaning at 20°C;

- Experimental procedure

First, we direct the device towards the light source then lift the prism, ensuring its glass surfaces are clean. The next step is to apply a few drops of the liquid sample onto the horizontal face of the reference prism using a pipette, this is done carefully to avoid contact between the pipette and the prism. Thereafter, we lower the prism while observing through the lower eyepiece and adjust the separation between light and dark zones using the right knurled button until it's clearly defined, then align this separation line with the reticle using the same button. The next step would be to read the refractive index value through the top eyepiece. Once the measurement is complete, raise the prism, wipe both surfaces clean with acetic acid, and close them gradually until the measurement for the next sample is taken.

$\mathbf{n_d^{20} = n_d^t + 0.00035\ (t-20)}$ **……………………………………………………Equation (5)**

where:

$\mathbf{n_d^{20}}$: refraction index at 20°C.

$\mathbf{n_d^{t}}$: refraction index taken at t temperature.

t : temperature at which the refractive index was measured

II.1.4 Density (ASTM D941) [61]

- Description of equipment

-Pycnometer

- Water bath
- Thermometer
- High-precision analytical balance

Figure III.4: Pycnometer

- Conditions of operating

- Specified test temperatures of 20 to 25°C. Its application is restricted to liquids having vapor pressures less than 80 kPa (600 mm Hg) and having viscosities less than 15 mm'/s (cst) at 20°C.

- Procedure

First, we weigh the empty pycnometer. Then, we fill it with distilled water at 4°C. After that, we put the filled pycnometer in a water bath for 15 minutes. Once it's out, we dry the outside, weigh it again to get the mass (m1).

Next, we fill the dry pycnometer with the petroleum product and put it back in the water bath for another 15 minutes. Lastly, we weigh it with the sample inside to get the mass (m2). To calculate the density of the oil sample, we use the formula:

d^{20}_{4}= (m2-m0)/ (m1-m0)……………………………………………………Equation (6)

where d^{15}_{4} is the density of the petroleum product at 20° C divided by that of water at 4°C, the reason for using water at this temperature is because density of distilled water at 4°C is 1.

III.1.5 VISCOSITY [62][63]

- Description of the equipment

-Ubbelohde viscometer

-Water bath

-Thermostat

-Thermometer from 15 to 120°C

-Stopwatch

- Mode of operating

- Sample is vigorously stirred and filtered into a clean and dry glass container through a sieve with a mesh opening of 75 µm; if necessary, remove water using an appropriate dehydrating agent.

- Load the Ubbelohde viscometer. To do this, we tilt the instrument approximately 30° from the vertical, with reservoir A below the capillary, then introduce enough liquid into tube 1 to bring the level up to the lower filling mark. The level should not exceed the upper filling mark when the viscometer is returned to the vertical position and the liquid has drained from tube 1. The lower U-tube should be completely filled without trapping air bubbles.

- When the viscometer has remained in the constant temperature bath for the required time (10 minutes at 40°C and 15 minutes at 100°C) to reach temperature equilibrium, open the third valve and draw liquid through the second tube until the liquid reaches the center of reservoir.

III.1.6 FTIR SPECTROSCOPY [64]

The presence of oxidation products is monitored by infrared spectroscopy. Oxidized sample of lube oil is investigated.

- Equipment description

Figure III.5: FTIR Spectrophotometer (SHIMADZU IRAffinity-1)

The various components comprising FTIR instrumentation include:

The Light Source: A broad-spectrum emitter, such as a mid-IR ceramic source, a far-infrared mercury lamp, or a near-infrared halogen lamp, serves as the source of illumination.

The Interferometer: At the core of an FTIR spectrometer lies the interferometer, consisting of a beamsplitter, a stationary mirror, and a moving mirror. The beamsplitter, a semi-transparent mirror, divides a collimated light beam into two optical paths. Half of the light is directed to the moving mirror while the other half is reflected to the stationary mirror. Both mirrors reflect the light beams, which are then recombined at the beamsplitter before passing through the sample chamber and reaching the detector.

The Sample: The beam enters the sample compartment where, depending on the analysis, it either transmits through or reflects off the sample surface. This is where specific frequencies of energy unique to the sample are absorbed.

The Detector: FTIR detectors convert transmitted or reflected light from the sample into electrical signals. The sensitivity and wavelength range of captured data are determined by the type and material of the detector. The detector transforms the beam into photons, which are further translated into measurable electric signals interpretable by the computer. Common detector types include room temperature DLATGS (Deuterated L-Alanine Doped Triglycine Sulfate) for regular analyses, cooled liquid nitrogen for sensitive applications, Si-photodiodes for near-IR and visible infrared applications, and silicon far-infrared bolometers.

-The Wavelengths are scanned in the range 600–4000 cm^{-1}

➢ Experimental procedure

- Turn on the FTIR spectrometer and allow it to warm up
    - A small sample is placed on a glass by pipette, while ensuring that it doesn’t touch the glass
    - The glass is then introduced to the spectroscopy
    - Set the appropriate measurement parameters such as the spectral range (wavenumber or wavelength), resolution, and number of scans.
    - Set the absorption spectrum as the spectrum we are investigating
    - Start the data acquisition process, then save and collect the spectrum shown by a disc.

III.1.6.1 Carbonyl index

From the carbonyl bands in the FTIR spectroscopy, a carbonyl index can be quantified. This is an index used to specifically monitor the carbonyl series during photo or thermo-oxidation processes by measuring the ratio of the carbonyl group with a reference band. [65]

Carbonyl index (CI)=$\frac{\boldsymbol{A(C=O)}}{\boldsymbol{A(CH2)}}$ *100

Where:

-C=O): Absorption peak under the band of carbonyls localized in the region 1650-1750 cm^{-1}.

-A (CH_2): Absorption peak under band reference group of methyl stretch in the region 1420-1500 cm^{-1}.

The reason for choosing CH2 as a reference band is due to its unchanging peak throughout the thermo-oxidation time.

III.1.7 UV VISIBLE [53]

- Description of equipment

Figure III.6: UV Visible Spectrophotometer (SHIMADZU UV-1900i)

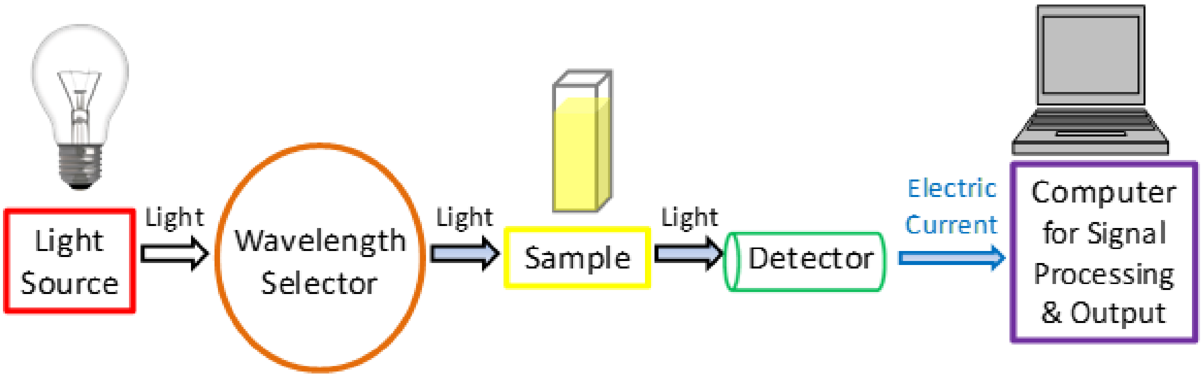

Figure III.7: A simplified description of how the UV visible spectrophotometry works [52]

A spectrophotometer has key parts as shown in figure 6: a light source, a monochromator, an absorption cell, a detector, and a signal processor. The light source gives out stable light. For UV light, it's hydrogen lamps; for visible light, it’s halogen lamps. The monochromator breaks down the light into specific wavelengths. It uses elements like prisms or gratings. Glass cells are for visible light, quartz for UV. Detectors measure the light passing through the sample, turning it into electrical signals using phototubes, photomultiplier tubes, or photodiode arrays. Spectrophotometers come in different types: single-beam or dual-beam based on their optical path, single-wavelength or dual-wavelength based on measurement method, and they can either scan spectra or use diode arrays for full spectrum detection.

- Experimental procedure

The apparatus was firstly turned on and left to warm for a few minutes about 10 minutes, then an empty cuvette is cleaned using distilled water and dried by a paper absorbent in the laboratory. Then put without samples of Los so we can use the spectroscopy as a reference, the after the cuvette is filled with samples starting with the virgin oil then cuvette is immediately introduced into the apparatus and closed then we adjust length to our desirable length of 200-400nm for every sample testes. Then the measurement was taken and recorded in a disk for analyses.

III.2 PART II RESULTS AND DISCUSSION

- DENSITY

As previously discussed in the second chapter, the density value is important in the analyses of LOs, used to monitor the quality and purity of lubricating oil, during its production and when setting its commercial value. Therefore, knowledge of density is very useful for carrying out mass balances and for calculating pump powers as well as analysing the degree of thermo-oxidation degradation. The density of virgin oil calculated in this project is using the equation (6). In figure III., the results show an increase of density with more time exposed to degradation with virgin oil having the density equal to 0.785021393, which was the smallest and the degraded having the highest of 0.81652036 , this could be due the polar compounds such as the aldehydes and ketones added during the oxidation process.[30] Moreover, the increase can also be associated with the formation of those high molecular weight materials that affects the molecular mass of the entire petrol together with the sludge added during polymerization [43], the increased molecular mass that affects directly the density as seen from the equation of how we calculate density.

For distilled water m0= 13.2674g   m1=18.6898g

Table 3: Experimental results of density versus time extracted from the measured mass

SAMPLE	D1(g/cm^3)	D2(g/cm3)	D3(g/cm3)	AVERAGE(g/cm3)	SD
VO	0.78548244	0.78544556	0.78568531	0.78553777	9.83574E-05
T6	0.79931396	0.79874225	0.79866849	0.79890823	0.000270483
T12	0.80943862	0.80785261	0.81587489	0.81105538	0.003213009
T24	0.81237091	0.81237091	0.81262909	0.81245697	0.00011475
T36	0.8128504	0.81292417	0.81351431	0.81309629	0.000278679
T48	0.81443641	0.81493435	0.81493435	0.81476837	0.000221304
T72	0.81602243	0.81607775	0.8159671	0.81602243	3.6884E-05
WO	0.81635438	0.82199764	0.81867808	0.81901003	0.001991738

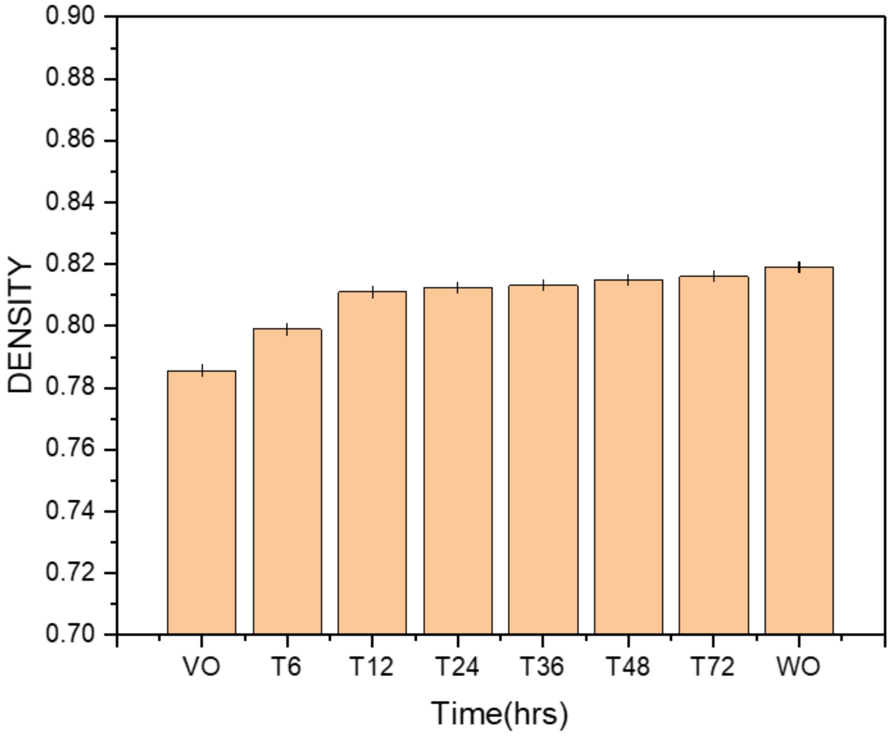

Figure III.8: Variation of density of Total Quartz 7000S 10W40 oil and time exposed at uniform to heat and air.

Furthermore, it can also be deduced from the results that the increase in density was the more significant between T6 and T12, the increase became slightly visible thereafter with a difference of ≤ 0.01. T48 and T72 showed similar results of 0.814436412, which can be reasoned that the thermo-oxidation degradation process was stabilising. However, the density was still different from the degraded sample although the difference is 0.002083948 which very small.

- FTIR SPECTROSCOPY

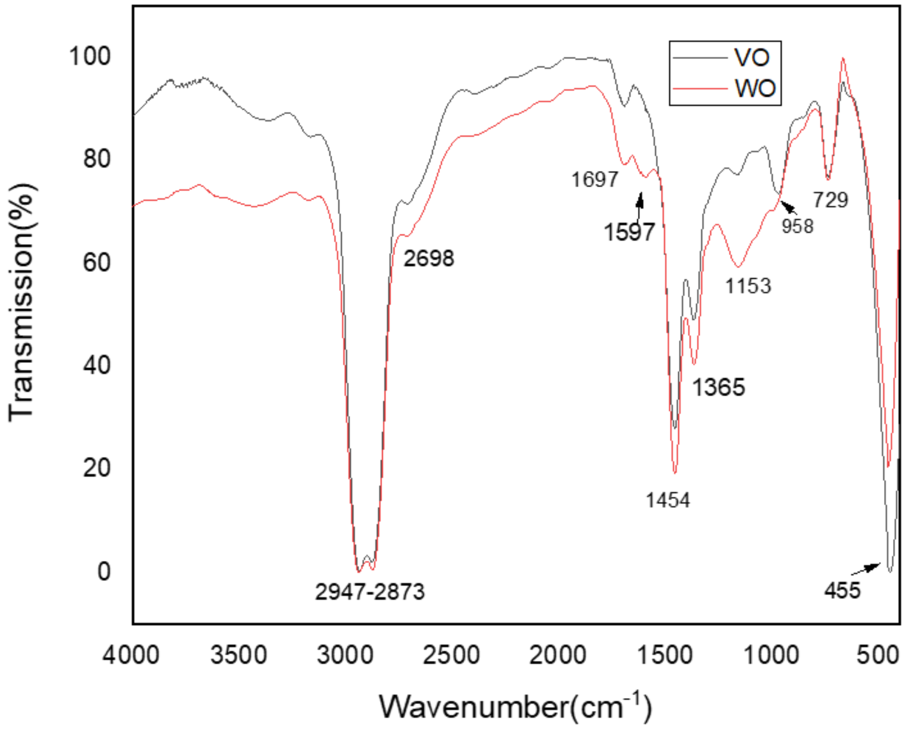

Figure III.9: Comparative FTIR Spectrum graphs of Virgin and Wasted oil of Total Quartz 7000S 10W40

The FTIR spectrum of lubricating oils was qualified by identifying the different transmittance bands present on each of the wasted and virgin oil spectrums. From figure III.8, it is evident that the two spectrums are almost identical with little differences, with the virgin oil having the highest transmittance percentage with short and broad bands than that of the wasted oil, which shows very low percentage of transmittance with long and thin bands. The similar bands identified for both oils they have peaks of ranging from 2950-3000 cm^{-1}indicating the presence of C-H stretch in aliphatic hydrocarbons, furthermore, there is immediately a C-H stretch of in unsaturated hydrocarbons observed at 2698 cm^{-1}. The observation is corroborated by the CH_2 bend at 1454 cm^{-1}, CH_3 bend is identified at 1365. According to [31] **,** on their study on mineral lubricants after thermal degradation, they revealed that aliphatic CH_3 are a representation of the presence of ketones, which was discussed in chapter 2 as products of chemical reactions for thermos oxidation. Moreover, the study conducted by [28] authenticate this observation and state that the bands indicate the presence of short-chained compounds with carbonyl groups from esters, ketones, or acids. The shifting of CH_2 symmetric stretching bands is less pronounced, likely because CH_2 groups are primarily attached to saturated carbons in the samples [66]. In the same research it was stated that this observation could further be verified with the formation of 1153 cm^{-1} as shown in figure III.8. Additionally, there is a recognition of C-H bending out of plane deformation in aromatic compounds. A new band formation for the WO at 1597 for the aforementioned peaks, they pose common functional groups however, their intensity of absorbance is what distinguishes them from the other, and there is a subtle shift in wavenumber as much as they belong to the same functional group. These small differences suggest potential degradation or alteration of chemical bonds in the wasted oil. Further investigation can be carried out to fully understand the implications of these findings for the performance and longevity of the lubricant oils in practical applications. Between 4000-3500 cm^{-1} a band bending inwards in WO specifically at 360 cm^{-1} which is assigned to the depletion of phenols in antioxidant which were described in chapter I as crucial in the hindering of oxidation process [67].The 729 band is linked to nitration as a thermos oxidation process described in chapter II, this according to [68], results from the oxidation of nitrogen oxide compounds.

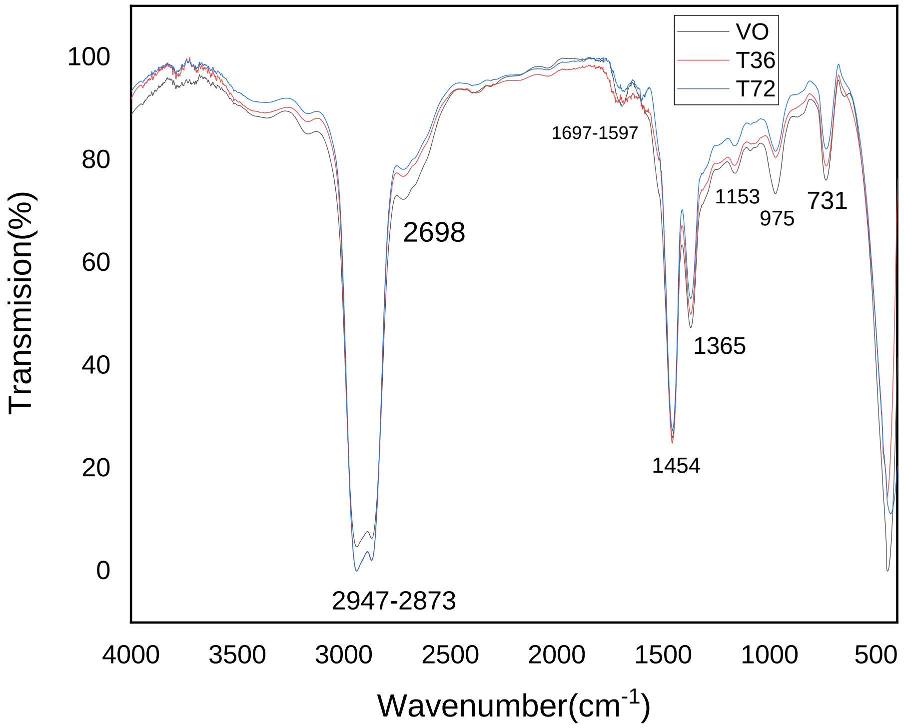

Figure III.10 (a) Combined FTIR Spectroscopies of LO under different time exposure to thermal and oxidation degradation

Figure III.9 is a comparative study of the evolution of transmittance bands for our Total Quartz 7000s 10W40 oil exposed over different periods to degradation. As in figure III.8, the transmittance bands are almost similar to the one with the VO however; the one noticeable difference is in the wavenumber stretch and transmission percentage. The results displayed a noticeable trend of becoming wider and longer at the same time dislocation of bands' wavenumber with prolonged exposure to thermal and oxidative stresses. For instance, the C-H stretch in VO is ranging from 2964-2834 cm^{-1}, whilst it starts at 2968 cm^{-1} for both T6 and T12 and for T72 it has greatly shifted to 2974cm^{-1}. This phenomenon is consistent with findings from previous studies on Kinetic Study of the Thermo-Oxidative Degradation of Squalane (C30H62) Modelling the Base Oil of Engine Lubricants [43] , where they stated that the oil bands of oxidation increase with the test duration.The hydroxyl group is not alternated at all in every spectrum. The variations in intensity fluctuations observed in the transmittance values at 1697 cm$^{-1,}$ 1153 cm−1, and 958 cm−1 indicate changes in the viscosity improvers and wear-resistant additives as they undergo aging.[67]

Deconvolution and assignment of bands in the 3000-2750 cm−1 region

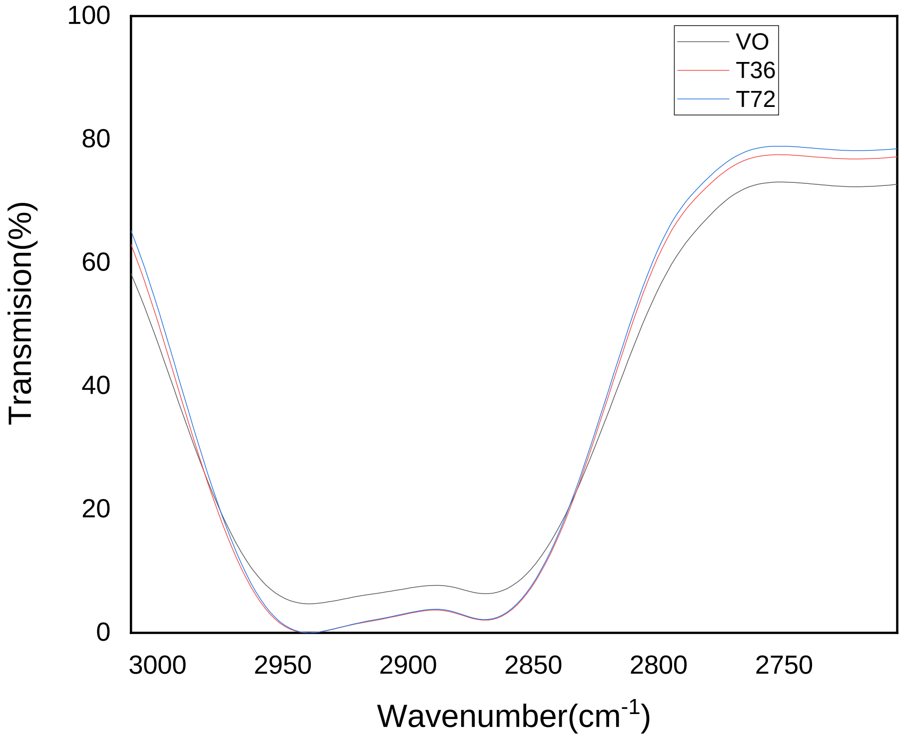

Figure III.10 (b): Evolution of band transmission of C-H Stretch

This part of the spectrum is known for showing the stretching vibrations of carbon-hydrogen (C-H) bonds in aliphatic compounds, which are typically the strongest bands in the spectra. In the studied samples, the bands represented different types of aliphatic groups like methyl, methylene, and methane. The bands at around 2954 and 2923 cm^{-1} are due to the stretching vibrations of asymmetric methyl and methylene groups, respectively. The band at 2897 cm^{-1} corresponds to the stretching of methine groups.

Symmetric stretching of methyl and methylene groups occur at lower wavenumbers, with bands at about 2869 and 2850 cm^{-1}, respectively.

There was a clear pattern between wavenumbers 4000-3000 cm^{-1} where the VO remained the one with the lowest transmittance percentage however it begins to shift from bottom to the highest at intervals 3000-2875 cm while the rest of the spectrum lines maintain their position. It slowly reverts to its position right after at the C-H stretch at around 2825cm^{-1}. The reason for this change can be attributed to the fact that VO being in its purest form possess a molecular structure with fewer impurities or alterations compared to the other oil samples. These impurities or alterations could lead to different vibrational modes or energy levels, affecting the absorption/transmission spectra at the C-H stretch bands.

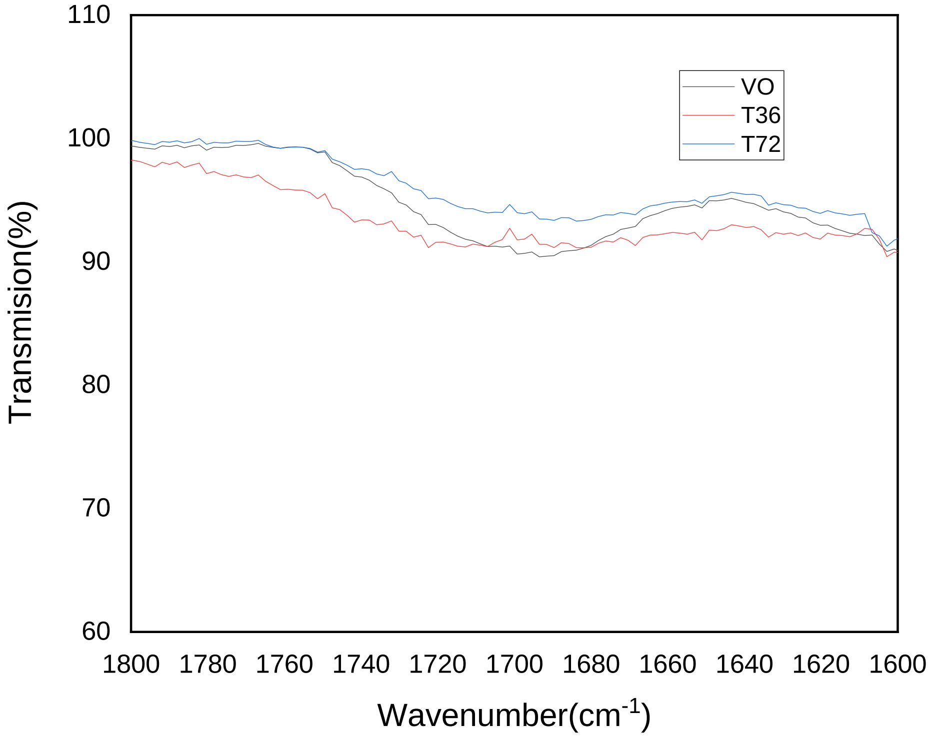

Figure III.10(c): Bands absorption bands in the carbonyl region

The range displayed in **Figure III.9(c)** is a range of carbonyl compounds such as ketones, carboxylique esters and acids, these are all chemical compounds resulting thermo-oxidation reactions discussed in the previous chapter. From the graph there is little peaks forming indicating the degree of oxidation especially in the carbonyls range at 1700 cm^{-1} C=O, the carbonyl groups formed as intermediate or end products of the degradation pathway of nitration reaction discussed in chapter 2 . This range can further be analysed quantitatively using carbonyl index.

CARBONYL INDEX

Table4: Carbonyl intensity bands and reference bands together with carbonyl percentage calculated

SAMPLE	A(C=O)	A(CH_2)	CI(%)
VO	0.33	0.73	45.2054795
T6	0.34	0.73	46.5753425
T12	0.35	0.73	47.9452055
T24	0.39	0.73	53.4246575
T36	0.42	0.73	57.5342466
T48	0.48	0.73	65.7534247
T72			

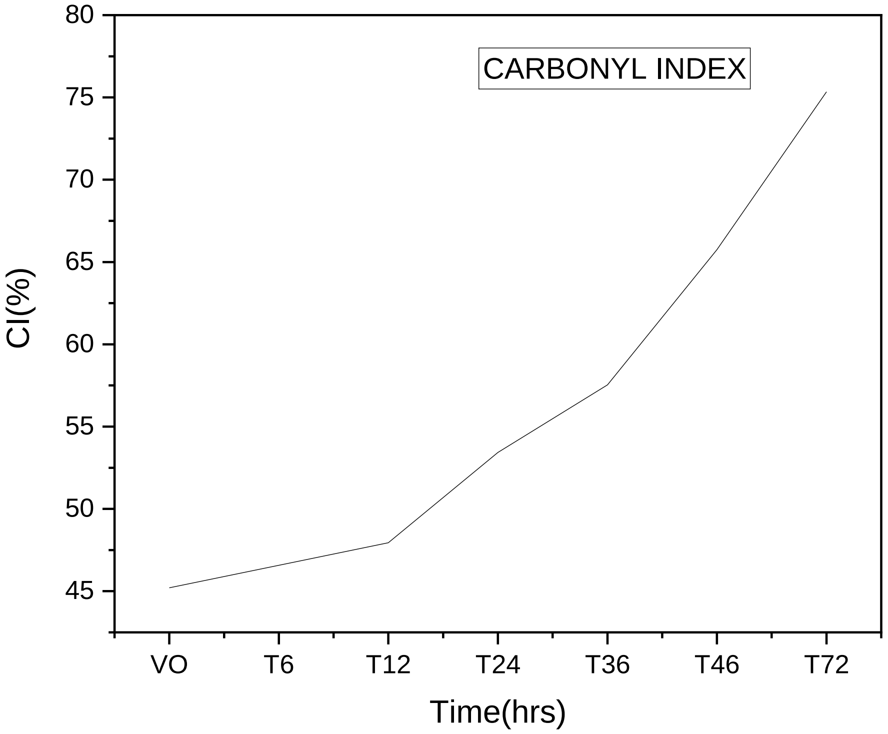

Figure III.11: carbonyl index graph variated with time from 0hrs to 72hrs of thermal oxidation exposure

The results of carbonyl index calculations on figure 5 at various time during thermal oxidation degradation provide insights into the progression of oil degradation over time. In our study, the carbonyl index increased gradually from an initial value of 45% at TO (VO) to 75% at T72, indicating a progressive degradation of the lubricant oil. The increase in the carbonyl index over time that we observed in our results is consistent with findings from previous studies on lubricant oil degradation. [69] reported similar trends in carbonyl index values during thermo-oxidative degradation of automotive lubricant oils. The rate of carbonyl index increase observed in our study may be influenced by various factors, including temperature, oxygen exposure, and the presence of metal catalysts. High temperatures during thermal oxidation promote oxidative reactions, accelerating the breakdown of hydrocarbon molecules and the formation of carbonyl compounds [70]. The presence of metal catalysts, such as iron and copper, further add to the thermo-oxidative degradation by catalyzing oxidation reactions and promoting the decomposition of hydro peroxides.

Based on this carbonyl index, a simple kinetic model presented by [71] aid us to estimate and calculate the global activation energy of the oxidation reaction in the simulation carried out in the lab. This model involves use of Arrhenius equation to help determine activation energy from the graph of ln (1-CI) versus time.

- UV VISIBLE SPECTROSCOPY

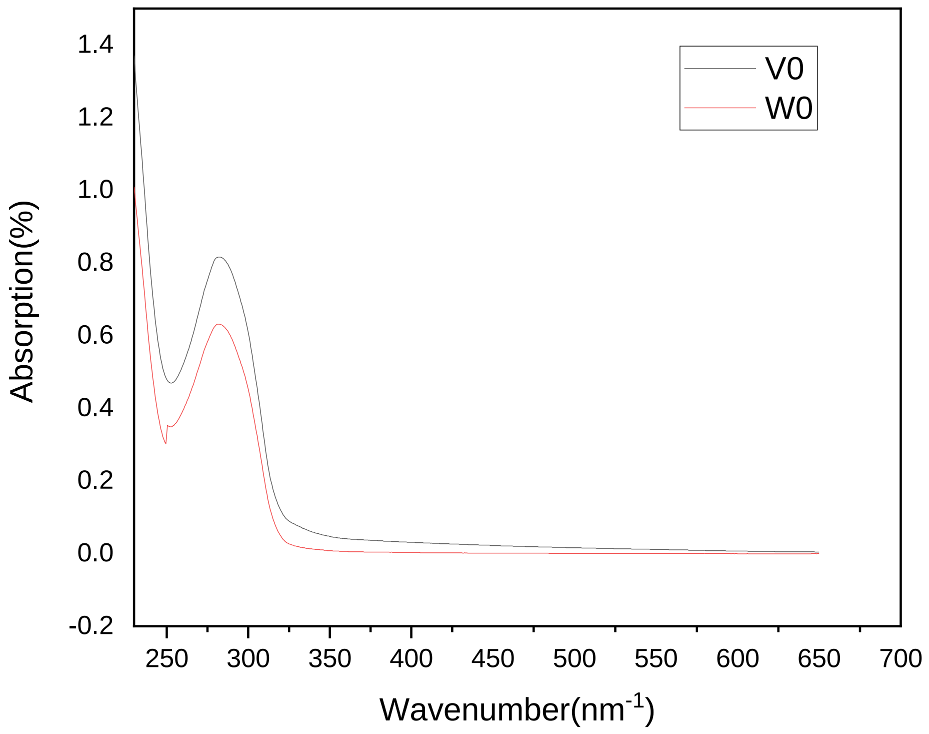

FIGURE III.12a: UV/Visible spectrum of wasted and virgin oil

Figure III.10a shows clearly that the highest value of the absorption spectrum A_{max} is 0.816% for the VO and 0.631% for WO, both at λ_{max}=282.5nm^{-1}. The absorbance at the wavelength range (330-590nm) represents minimum value absorbed. In the wavelength greater than 590nm^{-1} the absorbance takes approximately equal amounts of absorption intensities. The other difference displayed is in the change of the band around 250 nm^{-1} which is symmetric in VO and asymmetric in WO.

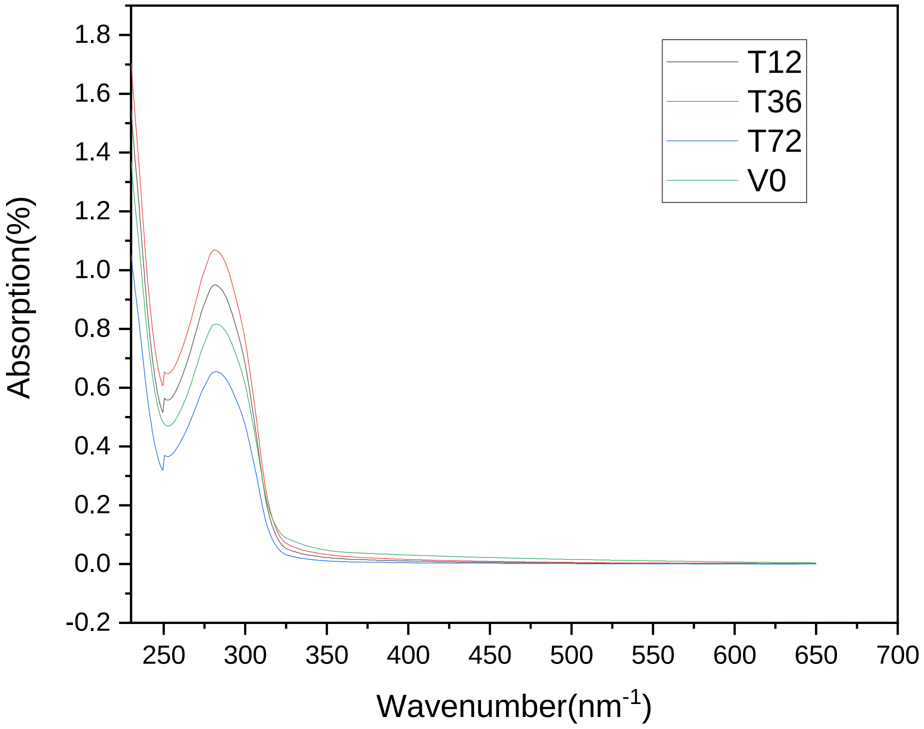

Figure III.12 (b): UV-Vis spectrum variation of absorption capacity over time

It is displayed in figure 5, the absorbance of lubricant oils at the 230–650 nm range clearly. The maximum wavelength being observed in the ultraviolet region specifically between 230 and 300 nm^{-1}, with a $\pi \rightarrow \pi^*$ transition [72]. There is a hyperchromic shift between T0- T48 and hypochromic shifts as time extends to T72 table 5 presents each value time with their exact value for the absorption intensities, which indicates the transformation upon ageing and begins to resemble that of the WO, this showed the increase in the byproducts of decomposition of LOs. However the other samples showed a lower absorption of molecules and according to [67], this is a result of the continued breakage of long chain hydrocarbon, therefore caused a lower absorption rate.

Table 5: Maximum bands of absorption in UV visible spectroscopy varied with time

SAMPLE OF LO	λ_{max}(nm^{-1})	A_{max}
T0(VO)	282.5	0.816
T6	282.5	0.895
T12	282.5	0.949
T24	282.5	1.027
T36	282.5	1.067
T48	282.5	1.160
T72	282.5	0.654
WO	282.5	0.631

Additionally, the absorption band between 230-250 depicts the presence of ketones, esters, acids and other oxidation products, which is seen to increase overtime denoting the extent of thermos oxidation as it increases overtime. The transition π → π * at wavelengths lower (<250 nm, high intensity with their conjugations, λmax ribbon π→ π * shifted to wavelengths greater and predictable with the Rules of Woodward.Pengan conjugation, the value of ε always be above 10,000. [72]

- REFRACTIVE INDEX

The refractive index of my 8 samples ranged from 1.688 - 1.5345, with the virgin oil having the highest refractive index and the degraded having the smallest as shown in figure 2. For their possession of high refractive index, it can be suggested that there is presence of aromatic compounds [28]. Degraded oil often contains higher levels of impurities compared to virgin oil, which can affect both absorption bands hence its refractive index properties.

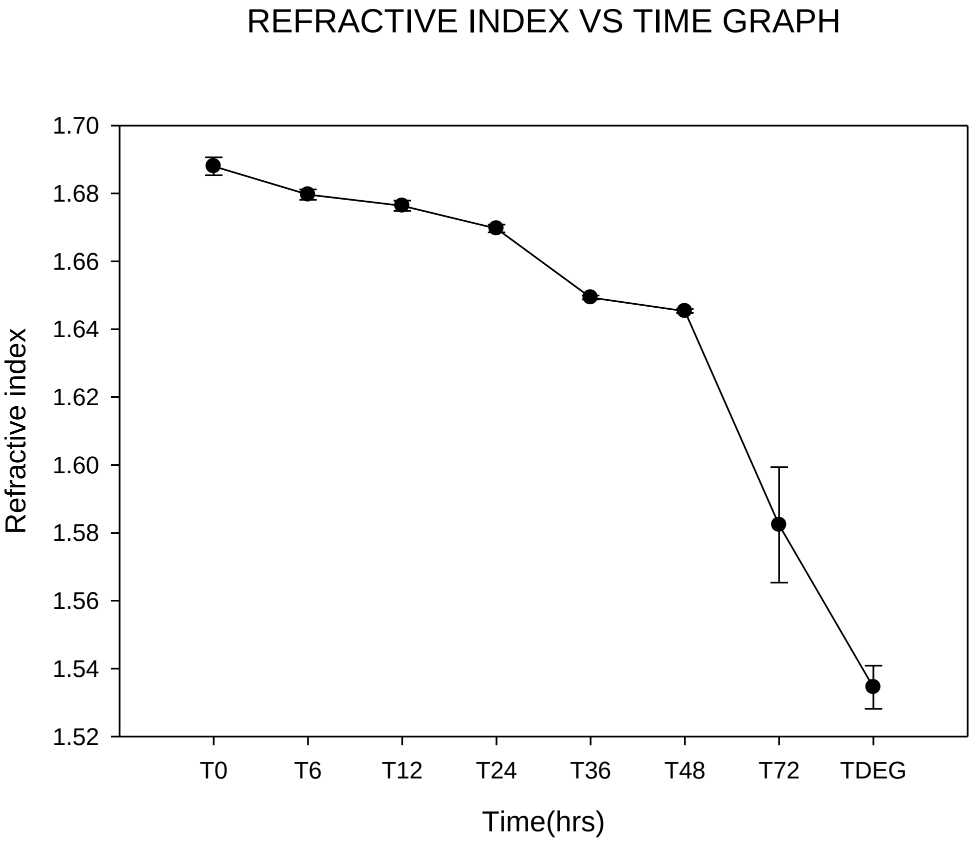

Figure III.13: The variation of refractive index with time taken to expose the LOs samples to uniform temperature and oxygen supply

The chemical changes that occur during the thermal and oxidation of oil alter molecular structures, new functional groups were formed and differences in purity, all of which are reflected in the optical and spectroscopic properties of the oils.

GENERAL CONCLUSION

GENERAL CONCLUSION

This project was investigating the process of thermo-oxidative degradation of lubricant oils, focusing on the effects of time and temperature alongside the role of additive technologies. The lubricant oil being studied had been simulated in the laboratory with accelerated ageing of constant temperature at 150°C, whereas time intervals were varied then characterised. Through comprehensive analysis, several key findings emerged:

- Thermo-oxidation was identified as the primary mechanism contributing to the degradation of lubricant oils, characterized by the formation of carbonyl groups detected via FTIR spectroscopy. Over time, transmission spectra exhibited a decrease, indicative of molecular structural changes. Our study highlighted the significant influence of temperature and oxygen exposure duration on the degradation process.
- UV-Visible spectroscopy revealed heightened absorption peaks, signaling the accumulation of oxidation by-products, while physical properties such as density increased due to molecular rearrangements.
- However, the refractive index decreased, suggesting alterations in the optical properties of the lubricant oils.
- Additive technologies were evaluated for their impact on mitigating thermo-oxidative degradation where in the uv visible spectroscopy, we would see LOs absorbing light at higher intensities overtime then slowly losing their ability over 72 hrs, to wasted oil which could be attributed to the depletion of additives therefore no longer having the ability to resist degradation. This characterization emphasized their crucial role in enhancing the oxidative stability and longevity of lubricant oils under harsh operating conditions.

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RESUME

L'usure d'une huile moteur est essentiellement liée à son oxydation qui a quatre conséquences directe: l'augmentation de la viscosité de l'huile, l'augmentation de l'acidité de l'huile, la formation de dépôts, vernis et boues et le noircissement de l'huile. Les conséquences sont alors analysées seules ou en combinaison, par des techniques de laboratoire basées sur des prélèvements périodiques. C'est dans ce contexte que ce projet se propose d’étudier la dégradation thermo-oxydative d'un lubrifiant de moteurs à combustion interne et plus particulièrement la cinétique de thermo oxydation en variant la température d'exposition. Les différents échantillons vieillis seront analysés par des techniques de mesure selon les standards imposés par les normes ASTM et par des techniques de mesure innovatrices qui détermineront l'état de la détérioration de l'huile en question. Des techniques de mesure telles que la spectrophotométrie IRTF et UV-visible, l’indice de réfraction, la densité etc. seront utilisée.

ABSTRACT

The wear of an engine oil is essentially linked to its oxidation which has four direct consequences: the increase in the viscosity of the oil, the increase in the acidity of the oil, the formation of deposits, varnish and sludge and oil blackening. The consequences are then analysed alone or in combination, using laboratory techniques based on periodic samples. It is in this context that this project aims to study the thermo-oxidative degradation of an internal combustion engine lubricant and more particularly the kinetics of thermo-oxidation by varying the exposure temperature. The various aged samples will be analysed by measuring techniques according to the standards imposed by ASTM standards and by innovative measuring techniques which will determine the state of deterioration of the oil in question. Measuring techniques such as FTIR and UV-visible spectrophotometry, refractive index, density etc. will be used